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DEVELOPMENT OF IMPROVED SOLDERS FOR ELECTRONIC RELIABILITY.(U)

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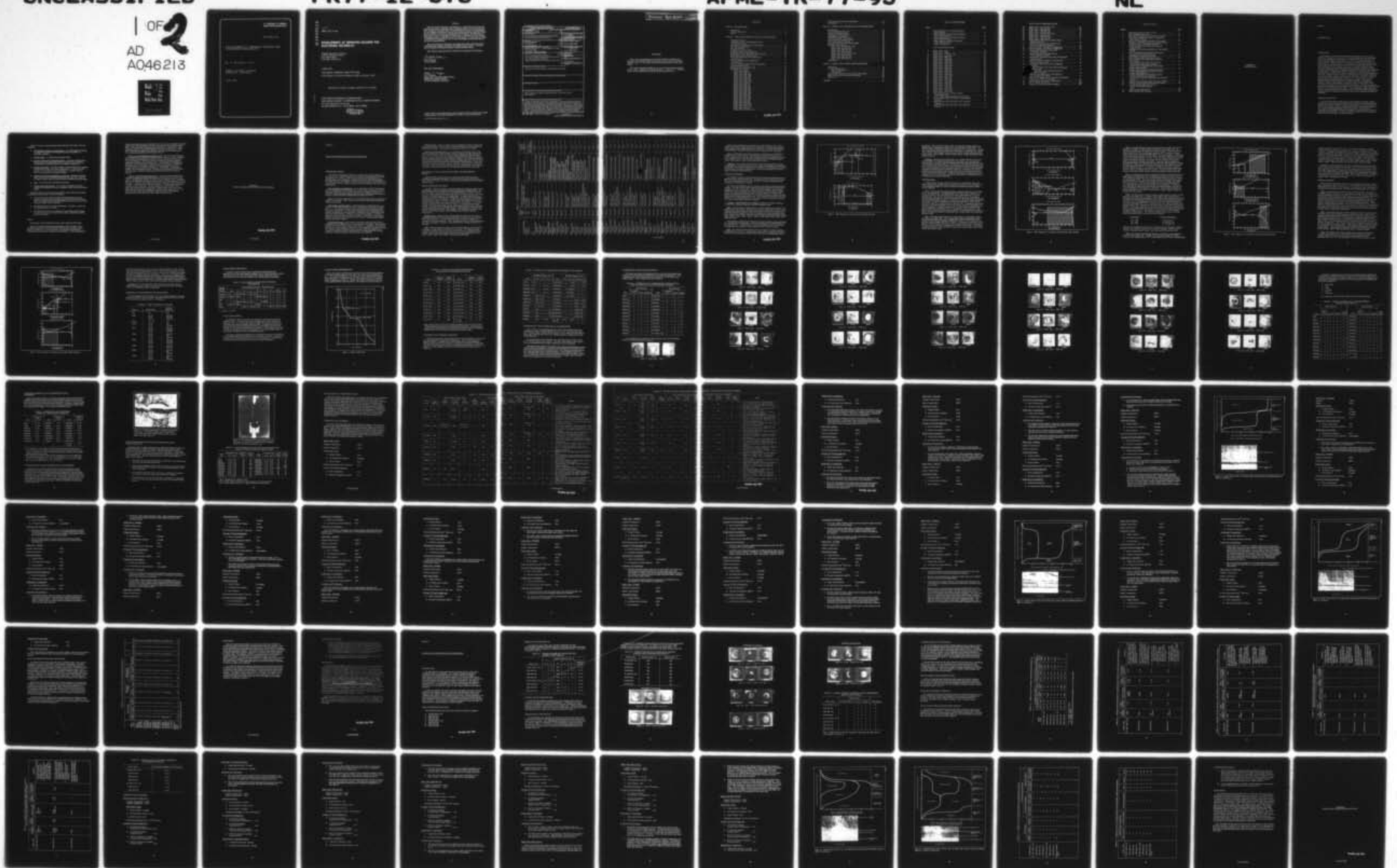

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M. C. Denlinger, et al

Hughes Aircraft Company
Fullerton, California

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Hughes Aircraft Company
Ground Systems Group
P.O. BOX 3310
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Final Report for Period 15 March 1976 to 12 April 1977

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AIR FORCE MATERIALS LABORATORY
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A higher temperature solder alloy intended for use on polyimide printed wiring boards was developed. The solder shows no evidence of cracking after exposure to 500 temperature cycles between 200°C and -55°C. A comparative test with Sn63 between 125°C and -55°C resulted in cracking after 200 cycles. The alloy (90Pb9Cd1Zn) was the result of selecting, testing and modifying all possible alloy systems that would be suitable for printed wiring board application. The resulting alloy, in addition to providing increased reliability, offers a significant cost reduction over the conventional tin-lead system.

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FOREWORD

This work was performed under Contract F33615-76-C5089 by the Materials and Processes Section of Hughes–Fullerton under the technical direction of Mr. D. W. Becker AFML/LLS Wright Patterson AFB, Ohio, 45433.

For Hughes Aircraft Company Mr. R. W. Korb was Program Manager and Mr. M. C. Denlinger was Project Engineer. Messrs T. O. Anderson and W. Smith assisted in the preparation and testing of alloys.

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Section 1

INTRODUCTION

BACKGROUND

Conventional tin-lead solder has been used exclusively in the electronics industry for many years. In spite of its many advantages and universal usage it has some significant disadvantages. In addition to its high cost which has been increasing rapidly in the past few years, it has limited resistance to thermal fatigue. Many instances of solder joint cracking have been observed. While some of these instances may be attributed to design deficiencies it would be advantageous to have a solder that is more resistant to thermal fatigue. Recent developments in polyimide materials have made it possible to extend the upper temperature limit of printed wiring boards beyond the range of eutectic tin-lead solder. Although it is difficult at this time to conceive of electronic applications that require higher service temperatures, the benefits of upgrading the solder could be indirect, similar to the benefits gained in using polyimide resins versus epoxy resins in circuit board materials. Presently, polyimides are used for their manufacturing advantages, e.g. less tendency to smear during drilling and less tendency to craze during rework. The indirect benefits of using a higher temperature solder compatible with polyimides should be economy and reliability. During the course of this study an alloy was found that possesses both of these characteristics. The alloy not only has phenomenal resistance to thermal fatigue and cracking but would be approximately 25% the cost of eutectic tin-lead solder. This development could be the first step in a significant advance for electronic assembly however the manufacturing methods need to be addressed before the system can be considered feasible for production.

PROGRAM OBJECTIVES

The primary objective of the program was to develop or modify a higher temperature solder alloy suitable for polyimide printed wiring board assembly. Meeting this primary objective involved establishing two sets of requirements. The first set (primary criteria) established the ability of candidate systems to meet desired physical properties of the solder itself. The second set (secondary criteria) applied to the processability of the alloy and its effect on manufacturing operations. Selection of candidate solders involved considering both sets of criteria which are discussed below.

Primary criteria, involving the physical properties of the alloy, were the following:

- Solderability to Copper, Gold and Kovar. The solderability rating had to compare to that of Sn 63 using fluxes that are acceptable for electronic assembly.
- Melting Range. A melting point less than 315°C.
- Service Temperature Approaching 200°C. The solder could not form undesirable intermetallics that cause a significant loss in physical strength after prolonged exposure to the service temperature.
- Mechanical Strength. Physical strength of solder joints had to compare with tin-lead at room and elevated temperature. At 125°C tin-lead has 40% of its strength at room temperature. A similar value at 200°C was expected for an improved solder.
- Electrical Resistivity Comparable to Tin-Lead. Although no specific limits were set tin-lead solders range from 13 to 20 x 10^{-6} ohm-cm. It would be expected that the improved alloy would fall within the range.
- Cost. The cost must be competitive with Sn 63.
- Toxicity and Health Hazards. The toxicity of candidate materials needed to be considered in terms of employee safety and environmental impact.

Secondary criteria, involving the processability of the alloy and its impact on manufacturing operations, were the following:

- The solder must be capable of being electrodeposited as an alloy. Printed wiring fabrication currently depends on the fact that tin-lead solder is codeposited by electrodeposition and serves as an etch resist during the copper removal process.
- The plating bath must not attack photoresist. Therefore, it must not be strongly alkaline or cyanide.
- The alloy should also be: (a) capable of being reflowed after plating; (b) solderable with non-corrosive fluxes; and (c) adaptable to reflow and wave soldering.

SCOPE

The program was accomplished in three major tasks described below:

Task I – Preliminary Selection and Screening – This task began with a thorough literature search and proceeded with a listing of possible systems based on melting point. All systems were reviewed from metallurgical, manufacturing and practical commercial considerations. From a preliminary

review, eight systems were selected for test. Alloys were prepared, chemically analyzed to verify composition, and then submitted for alloy characterization tests. Tests consisted of melting point determination, solderability, microstructural analysis, mechanical strength, and electrical resistivity. Alloys were screened according to their characteristics and overall performance. The most promising ones were selected for Task II.

Task II – Alloy Modification and Optimization – This task concentrated on alloy modification and refinement indicated by the results in Task I. Modification consisted of changing from a binary to ternary system and altering the ratio of constituents. This task was also to include the possible adding of impurities to achieve better wetting or flow. Consideration of tradeoffs and prediction of side effects were considered prior to actual alloy modification. Selected alloys were modified, subjected to chemical analysis to verify composition then examined for melting point, solderability, metallurgical stability, and mechanical strength. Results were compared with the tin-lead control system to select the most promising alloys for further testing in Task III.

Task III – Final Characterization Study – The final characterization study consisted of obtaining in depth information on alloys that were selected from Task II. Metallurgical stability was determined by exposing Kovar and copper ribbon leads soldered to polyimide circuit boards to thermal aging at 200°C for 500 hours. A control test using tin-lead coated boards was made with exposure to 125°C. Bond tests were made and compared. Metallurgical examination of bonds was also conducted. Thermal fatigue tests were performed by subjecting soldered leads to temperature cycling between 200°C and -55°C. Bond tests were made and compared to a control sample using tin-lead. The effect of shock loading was determined comparing boards with flatpacks soldered with the test alloys with those soldered with tin-lead.

SECTION 2
TASK I PRELIMINARY SELECTION AND SCREENING

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TASK I PRELIMINARY SELECTION AND SCREENING

PRELIMINARY SURVEY

The selection of alloys for inclusion in Task I of this study consisted of a two step survey. The preliminary survey consisted of an analysis of the characteristics of the solder in relation to its own inherent characteristics (i.e., melting range, cost, metallurgy, compositional range, and health hazards). The final selection encompassed a detailed analysis of alloys recommended from the preliminary survey. Factors considered in the preliminary survey are discussed below.

Flow and Service Temperatures – As a requirement, the flow temperature had been established at <315°C since polyimide printed wiring boards can withstand that temperature for moderate time periods. Metals and alloys that exhibit melting temperatures approaching the required flow temperature would, in theory, exhibit the better strength characteristics at 200°C.

Cost – The ultimate application for the proposed solder system is production printed wiring boards. Thus, material costs become important and high cost metals were avoided.

Metallurgical Characteristics – In the application of metals and alloys as solders, it was most desirable that simple metallurgical structures be considered, i.e., pure metals or binary alloys consisting of either solid solutions, eutectics or peritectics. Complex alloy systems that form undesirable intermetallic compounds were not included for candidacy due to the difficulties that result from such systems. Although not an absolute necessity, it would be desirable to plate the developed alloy onto PCBs. Therefore, the preliminary analysis was limited to pure metals or binary alloys, allowing further adjustments in alloying for Task II.

Compositional Range – Alloy systems exhibiting a wide potential range of compositions were considered the most desirable for this study. Also, specific compositions within an alloy system would allow for a reasonable compositional tolerance to permit production melting and, where applicable, production plating. For example, alloys exhibiting eutectic reactions where the liquidus line is extremely steep at the eutectic composition may be undesirable due to sharp variation in melting point with a slight change in composition.

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Health Hazards – Under presently enforced standards, employee safety and environmental impact become important considerations when developing future production processes. Consequently, highly toxic metals were avoided.

Results of Preliminary Survey – The results of a preliminary survey conducted to obtain pure metals and binary alloys exhibiting melting temperatures in the 200°C to 315°C range are shown in Table 1 along with other characteristics. As can be seen, two pure metals and thirteen alloys appear to exhibit certain characteristics that merited further analysis. The remaining candidates were not recommended for various reasons, including high cost, toxicity, poor compositional range and undesirable metallurgical characteristics. Each characteristic that was considered cause for rejection is underlined in the table for each entry. Note that the table includes only those intermetallic compounds that would be encountered at the specific compositions considered for each alloy.

DISCUSSION OF ALLOY GROUPS SELECTED IN THE PRELIMINARY SURVEY

Materials under consideration were organized in the following groups: (1) Bismuth and bismuth rich alloys, (2) tin and tin rich alloys, (3) lead-rich alloys and (4) cadmium-rich alloys. These various metal systems are discussed in detail below.

Bismuth and Bismuth Rich Alloys

Normally, bismuth is used as an alloying addition for specialty alloys including bearings, pattern reproduction and low melting alloys (fusible alloys). As shown in Table 1, pure bismuth has a melting temperature of 271°C; however, it is very brittle and has a high electrical resistivity (106.8 microhm-cm), both of which are disadvantages for PCB applications. A unique characteristic of bismuth is its volume expansion on solidification. The effect of such expansion on PCB's would require evaluation. No data is readily available on the wetting characteristics of pure Bi; however, fusible alloys containing 50-55 Bi do not readily wet pure copper and require a harsh flux to wet properly. To promote wetting, plating the base metal with tin, silver, or cadmium produces good results. It can be inferred that pure Bi would follow the same trend. Bismuth has only been plated on an experimental level, thus application to PWB's would require an alternate approach. With respect to intermetallic compound formation, Bi readily forms Au_2Bi, NiBi and $NiBi_3$ at the expected soldering temperature.

Bismuth Alloys – Since all three alloys listed are extremely rich in Bi, it would follow that much of the foregoing discussion would be true for the alloys. Electrical resistivity, if it follows normal behavior, would be expected to increase with alloying additions. Also, alloying would tend to reduce brittleness and volume expansion. However, at the high Bi level, wetting would still be a problem.

BiSb – Bismuth-antimony exhibits a solid solution diagram with the desired temperature range located at 94-100 Bi (wt. percent). The highest liquidus temperature (315°C) would be achieved at 94% Bi with a corresponding 280°C solidus. Intermetallic compounds that could form when soldering Au, Cu or Kovar include Au_2Bi, NiBi, $NiBi_3$, $AuSb_2$ and possibly $NiSb_2$.

TABLE 1. PRELIMINARY SURVEY LISTING OF ALLOYS

Potential Solder	Melting Range (^{o}C)	Metallurgical Characteristics of Potential Solder Alloy	Other Remarks	Possible Further Analysis
Bismuth	271	Pure Metal		Yes
Thallium	303	Pure Metal	Very Toxic	N.R. (Not Recommended)
Tin	232	Pure Metal		Yes
Silver-Bismuth (Ag-Bi)	262-315	Eutectic at 97.5 Bi	Reasonable Compositional Range	Yes
Silver-Lead (Ag-Pb)	304-315	Eutectic at 97.5 Pb	Reasonable Compositional Range (1 Alloy)	Yes
Silver-Tin (Ag-Sn)	221-315	Eutectic at 96.5 Sn IMC – Ag_3Sn	Reasonable Compositional Range (1 Alloy)	Yes
Silver-Thallium (Ag-Tl)	291-315	Eutectic at 98.5 Tl	Tl very toxic Limited Compositional Range	N.R.
Aluminum-Tin (Al-Sn)	228-315	Eutectic at 99.5 Sn	Limited Solubility. Requires Close Compositional Control	N.R.
Arsenic-Bismuth (As-Bi)	270-315	Eutectic at <1 As	As-very toxic. Limited Compositional Range	N.R.
Arsenic-Lead (As-Pb)	288-315	Eutectic at 2.8 As	As-very toxic. Limited Compositional Range	N.R.
Gold-Bismuth (Au-Bi)	241-315	Eutectic at 82 Bi IMC – Au_2Bi	Wide Compositional Range (Multiple Alloys). Unpredictable Gold Costs	N.R.
Gold-Cadmium (Au-Cd)	309-315	Eutectic at 87 Cd IMC – $AuCd_3$	Reasonable Compositional Range Au Cost - Unpredictable	N.R.
Gold-Lead (Au-Pb)	215-315	Eutectic at 85 Pb IMC – $AuPb_2$	Wide Compositional Range Au Cost – Unpredictable	N.R.
Gold-Tin (Au-Sn)	215-315	Eutectic at 90 Sn IMC – Au Sn, Au Sn_2, Au Sn_4	Wide Compositional Range Au Cost - Unpredictable	N.R.
Bismuth-Lead (Bi-Pb)	220-315	Solid Solution Portion of Eutectic (>82 Pb)	Wide Compositional Range (Multiple Alloys)	Yes
Bismuth-Zinc (Bi-Zn)	271-315	Solid Solution	Reasonable Compositional Range	Yes
Bismuth-Palladium (Bi-Pd)	256-315	Eutectic at 3 Pd IMC – Bi_2 Pd	Narrow Compositional Range	N.R.
Bismuth-Rhodium	269-315	Eutectic at <1 Rh	Narrow Compositional Range	N.R.

Bismuth-Lead (Bi-Pb)	220-315	Solid Solution Portion of Eutectic (>82 Pb)	Wide Compositional Range (Multiple Alloys)	Yes
Bismuth-Zinc (Bi-Zn)	271-315	Solid Solution	Reasonable Compositional Range	Yes
Bismuth-Palladium (Bi-Pd)	256-315	Eutectic at 3 Pd IMC – Bi_2 Pd	Narrow Compositional Range	N.R.
Bismuth-Rhodium (Bi-Rh)	269-315	Eutectic at <1 Rh IMC – Bi_4 Rh (Apparent)	Narrow Compositional Range	N.R.
Bismuth-Zinc (Bi-Zn)	255-315	Eutectic at 97 Bi	Reasonable Compositional Range	Yes
Bismuth-Selenium (Bi-Se)	270-315	Eutectic at <1 Se IMC – Bi_2 Se	Narrow Compositional Range	N.R.
Bismuth-Tellurium (Bi-Te)	266-315	Eutectic at 1.5 Te IMC – Bi_{14} Te_6, Bi_2 Te	Narrow Compositional Range	N.R.
Cadmium-Copper (Cd-Cu)	314-315	Eutectic at 99 Cd IMC – Cu Cd_3	Narrow Compositional Range	N.R.
Cadmium-Lead (Cd-Pb)	248-315	Eutectic at 83 Pb	Wide Compositional Range (Multiple Alloys)	Yes
Cadmium-Antimony (Cd-Sb)	285-315	Eutectic at 95 Sb IMC – Cd_3 Sb_2	Reasonable Compositional Range	Yes
Cadmium-Thallium (Cd-Tl)	204-315	**Eutectic at 83 Tl**	**Tl very toxic** **Wide Compositional Range**	N.R.
Cadmium-Zinc (Cd-Zn)	266-315	Eutectic at 17 zn	Wide Compositional Range (Multiple Alloys)	Yes
Copper-Tin (Cu-Sn)	227-315	Eutectic at 99 Sn IMC-$Cu_6$$Sn_5$	Narrow Compositional Range	N.R.
Indium-Lead (In-Pb)	220-315	Solid Solution Portion of Peritectic (>50 Pb)	Wide Compositional Range (Multiple Alloys)	Yes
Indium-Thallium (In-Tl)	220-303	**Solid Solution Portion of Diagram (>80 Tl)**	**Tl-toxic** **Wide Compositional Range**	N.R.
Lead-Palladium (Pb-Pd)	265-315	Eutectic at 95 Pb IMC – Pd Pb_2	Narrow Compositional Range	N.R.
Lead-Platinum (Pb-Pt)	290-315	Eutectic at 95 Pt IMC – Pt Pb_4	Narrow Compositional Range	N.R.
Lead-Antimony (Pb-Sb)	252-315	Eutectic at 11 Sb	Wide Compositional Range	Yes
Lead-Tin (Pb-Sn)	280-315	Solid Solution Portion of Diagram (>84 Pb)	Wide Compositional Range	Yes
Lead-Thallium (Pb-Tl)	301-310	Peritectic Area	**Tl - very toxic** **Reasonable Range**	N.R.
Antimony-Tin (Sb-Sn)	246-315	Peritectic at 10-42 Sb	Reasonable Compositional Range	Yes
Tin-Thallium (Sn-Tl)	250-302	Solid Solution Area of Eutectic (>83 Tl)	**Reasonable Compositional Range** **Tl - very toxic**	N.R.

2

BiAg – The bismuth-silver system forms a single eutectic at 95.7 Bi at 262°C. Hypoeutectic alloys reach 315°C liquidus at 93 Bi while hypereutectic alloys approach the melting point of pure Bi (271°C). Potential intermetallics on soldering are limited to those formed with Bi (Au_2Bi, NiBi, and $NiBi_3$).

BiZn – The bismuth-zinc system includes a monoeutectic at 416°C and an eutectic at 254.5°C (97.3% Bi). The hypoeutectic alloys reach a liquidus of 315°C at approximately 94% Bi while the hypereutectic alloys approach the melting temperature of Bi. Potential intermetallics formed on soldering include Au_2Bi, NiBi, $NiBi_3$, $AuZn_8$, $NiAn_8$ and possibly $AuZn_8$.

Summary – As a result of the analysis of bismuth and bismuth-rich alloys for application to improved solders, it was decided that further consideration be terminated. The extremely high electrical resistivity, brittleness, poor wetting characteristics and lack of plating history make them unattractive for solder alloys for advanced PCB fabrication.

Tin and Tin-Rich Alloys

Tin exhibits a number of characteristics that warrant its consideration for a high temperature soldering material. Its melting point of 232°C permits possible use to temperatures in the vicinity of 200°C. Tin also is plateable, thus allowing direct application to PCB's.

The electrical resistivity of tin (11 microhm-cm) also is a favorable characteristic. The use of tin for high temperature solders results in certain disadvantages that must be overcome. These include its tendency, under certain conditions, to form whiskers, thus causing shorting on a PCB and a propensity to form intermetallic compounds with the various metals to be joined. The growth of whiskers can be alleviated by "poisoning" the pure tin with an alloying element such as lead (approximately 1%). Other elements may achieve the same benefits and, if selected properly, could also increase the melting temperature thus improving elevated temperature strength.

Sn Alloys – Phase diagrams for candidate tin alloys are shown in Figure 1; the desired compositional range is indicated by shaded areas.

SnSb – The tin-antimony system (view a) exhibits a peritectic reaction in the desired temperature range. The peritectic occurs at 246°C and 10.5% Sb. In all compositions within the desired range, the solidus temperature increases from 232°C (Sn melting temperature) to the 246°C peritectic, thus a potential exists for an increase in strength. Expected compounds during soldering include $AuSb_2$, AuSn, $AuSn_2$, $AuSn_4$, Cu_3Sn, Cu_6Sn_5, $FeSn_2$, Ni_3Sn_4 and possibly $NiSb_2$, FeSn, CoSn and $CoSn_2$.

Commercially available 95 Sn-5Sb alloy is usually used for improved strength over conventional tin-lead solder. Electrical resistivity of 95 Sn-5Sb solder is 14.5 microhm-cm. A disadvantage is the lack of plating history for antimony. Although baths are available, it is presently not done in large volumes.

SnAg – The tin-silver phase diagram (view b) exhibits an eutectic transformation at 96.5 Sn of 221° C. Hypoeutectic alloys achieve a liquidus temperature of 315°C at 89 Sn while hypereutectic alloys approach the melting point of pure

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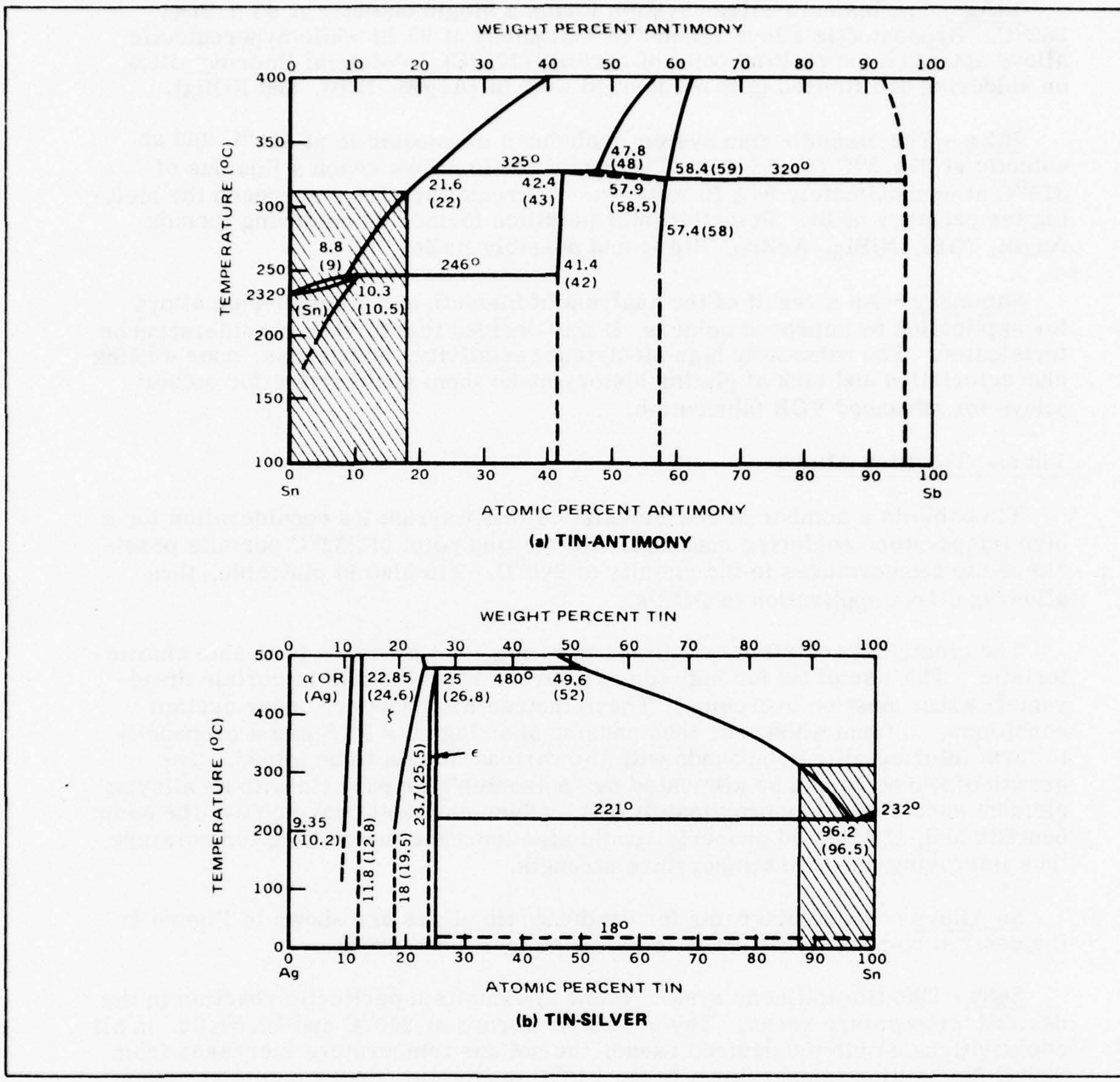

Figure 1. Phase Diagrams for Tin Binary Systems SnSb and SnAg

Sn (232°C). Commercial tin-silver alloys are generally stronger and have a slightly higher temperature capability than conventional tin-lead solder. The 95 Sn-5Ag alloy exhibits good electrical resistivity (10.4 microhm-cm). In addition, alloy plating would be possible with this system, an advantage for application to PCBs. Intermetallic compounds expected from solder operation would include AuSn, $AuSn_2$, $AuSn_4$, Cu_3Sn, Cu_6Sn_5, $FeSn_2$, Ni_3Sn_4 and possibly FeSn, CoSn and $CoSn_2$.

Summary – Based on the foregoing data, two metals of the Sn-rich system were selected for evaluation during Task I of this study: pure tin and a tin-antimony alloy. The only major disadvantage foreseen is the high potential for intermetallic compound formation. An approach to alleviate this situation would be to coat the Kovar with the solder alloy developed as opposed to gold plating as in the current practice on many flat-pack leads where tin or tin-lead solder has replaced gold plated leads for production soldering. In addition, the possible formation of intermetallics with iron and nickel has been controlled for the currently available tin coated leads. Although exhibiting many outstanding characteristics, the tin-silver system was rejected from further consideration due to its relatively low melting temperature.

Lead Rich Alloys

A large number of lead-rich solder families are available for this study. Phase diagrams for potential binary systems are shown in views a through c of the accompanying Figures 2 and 3 with desired compositional ranges shaded on each diagram.

PbAg – The lead-silver system exhibits an eutectic reaction at 97.5 Pb and 304°C (see Figure 2a). The liquidus slopes are quite steep, reaching 315°C at approximately 97 Pb on the hypoeutectic and at approximately 98.5 on the hypereutectic, thus only one nominal alloy composition can be investigated. Commercially available 97.5 Pb/2.5 Ag solders are somewhat less wettable than conventional SnPb eutectic solder, primarily due to the poor wetting characteristics of lead. The alloy exhibits good mechanical properties to 175°C and its electrical resistivity is reported at 19.5 microhm-cm. Consideration must also be given to corrosion resistance of the PbAg system since it is susceptible to a humid atmosphere. Improved resistance to corrosion would be desirable and can be achieved by the addition of tin. An advantage to this system for PCB applications is that both elements can be plated. On soldering to gold, copper or Kovar, potential intermetallic compounds formed would include only $AuPb_2$ and possibly Au_2Pb.

PbBi – The lead bismuth system is a solid solution at the desired temperature range (see Figure 2b). The corresponding compositional range is from 95 Pb to 85 Pb where the liquidus changes from 315°C to 285°C with a corresponding solidus change from 290°C to 230°C. Little data are available for this system, however based on the poor wetting characteristics of pure lead and pure bismuth, this alloy system would apparently exhibit poor wetting. Intermetallic compounds expected to form at solder temperatures include Au_2Bi, NiBi, $NiBi_3$, $AuPb_2$ and possibly Au_2Pb.

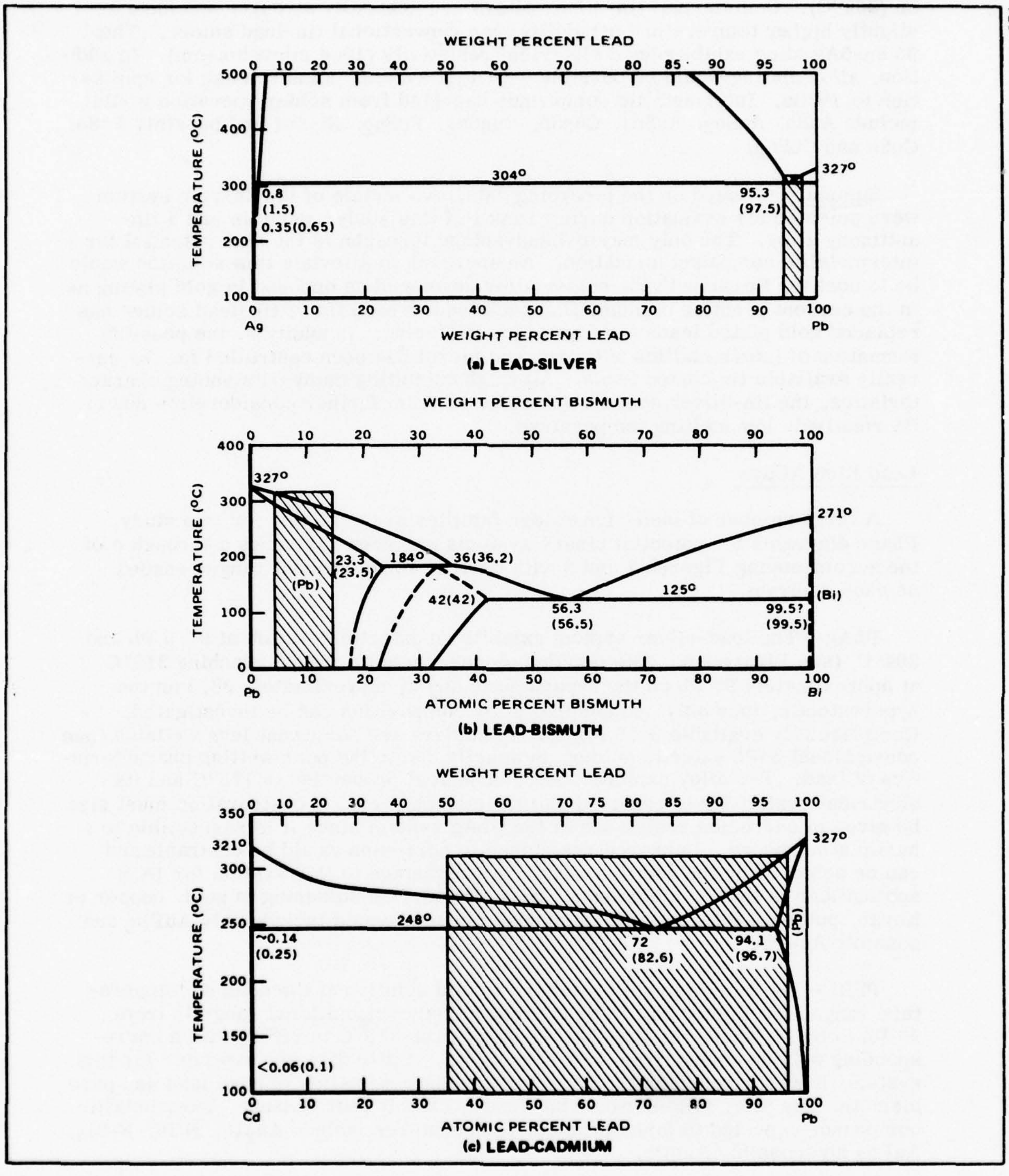

Figure 2. Phase Diagrams for Lead Binary Systems PbAg, PbBi and PbCd

PbCd – The lead-cadmium system forms an eutectic at 248°C and 82.6 Pb, and covers virtually the entire range of composition (see Figure 2c). The liquidus temperature for the hypoeutectic reaches 280°C at 50 Pb while at the hypereutectic (96.7 Pb) it reaches approximately 300°C, therefore a broad range of alloys with a common solidus (248°C) can be investigated. Further, at compositions higher than 96.7 Pb, the solidus increases to approximately 280°C with a corresponding liquidus of 315°C. Very little engineering data are available for this system; however, it is known that the presence of Cd in SnPb solders can promote tarnishes and oxides. This alloy system exhibits two potential advantages: (1) both elements can be plated, thus application to PCB's is simplified, and (2) the relatively high melting range may result in adequate strength approaching 200°C. No data are available on electrical resistivity. Pure Cd exhibits a value of 6.8 microhm-cm, which will increase on alloying; however, such a low initial value is promising. Expected intermetallic compounds would include $AuCd_3$, $CuCd_3$, $AuPb_2$ and possibly Cu_5Cd_8 and Au_2Pb.

PbIn – The lead-indium system exhibits solid solution in the desired temperature range (see Figure 3a), with the liquidus increasing from 240°C (Pb) to 315°C (approximately 95 Pb) with a corresponding solidus increase from 220°C to approximately 310°C. Some commercial alloys are available in this range, however electrical resistivity values indicate that they are higher than SnPb (14.5 microhm-cm). The 75 Pb/25 In alloy has an electrical resistivity of 37.5 microhm-cm while 95 Pb/5 In exhibits 33.8 microhm-cm. It should be noted that both Pb and In can be plated from fluoborate solutions, thus there is a good possibility of alloy plating (as with PbSn). Intermetallic compounds at solder temperatures are expected to include AuIn, Ni_2In_3, Ni_3In_7, $AnPb_2$ and possibly AuIn and Au_2Pb.

PbSb – The lead antimony system exhibits a single eutectic reaction at 252°C and 11 Sb (see Figure 3b). A relatively wide range of alloy compositions is available with varying melting ranges. At the eutectic temperature limit (3.5 Sb) the liquidus is approximately 305°C while the hypereutectic liquidus approaches 315°C at 19 Sb. At compositions lower than 3.5 Sb, the solidus temperature increases to approximately 300°C at approximately 2 Sb while the liquidus is at approximately 315°C. Antimony is commonly added to pure lead to increase its strength, commercial alloys being hard lead (4 Sb and 6 Sb) and antimonial lead (9 Sb). An interesting phenomena in the Pb/4 Sb alloy is an apparent age hardening (ASM Handbook, Vol. 1, 8th Edition), which may prove to be of distinct advantage in this program. The ultimate strength achieved was 11,000 psi. Electrical resistivities for these alloys are as follows:

Composition	Electrical Resistivity
Pb – 4 Sb	24 microhm-cm
Pb – 6 Sb	25 microhm-cm
Pb – 9 Sb	27 microhm-cm

Adding to the advantages of this alloy is its potential for being plated. Although antimony is not plated in large volume, a bath is available. Expected intermetallic compounds include $AuPb_2$, $AuSb_2$ and possible $NiSb_2$ and $CoSb_3$.

PbSn – The desired compositional range for the lead-tin system appears at 84 to 96 Pb (see Figure 3c). Through this compositional range the solidus increases from approximately 220°C to approximately 310°C with a corresponding

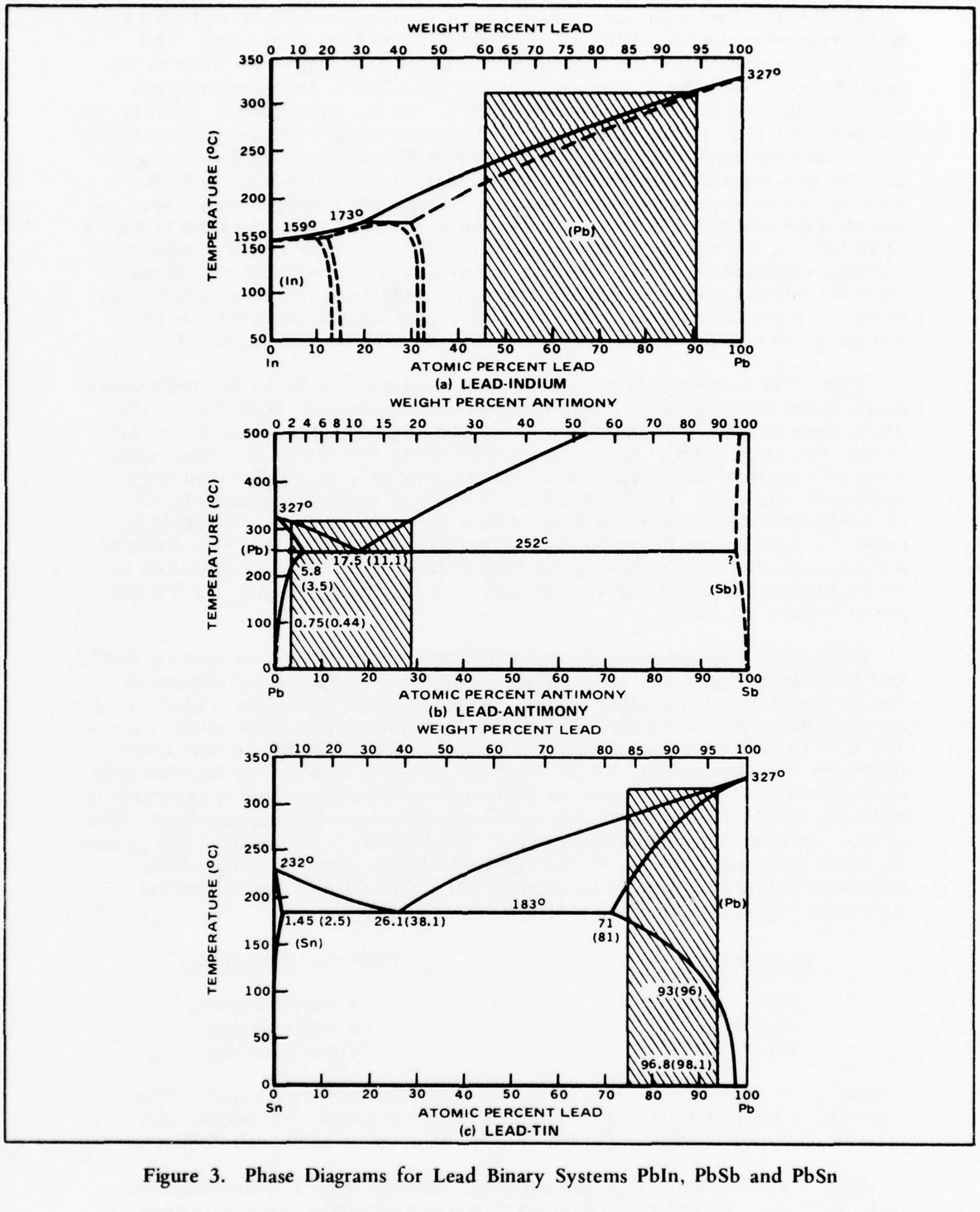

Figure 3. Phase Diagrams for Lead Binary Systems PbIn, PbSb and PbSn

liquidus increase from 280°C to 315°C. An elevated temperature melting range of this type appears promising for the retention of strength in the region of 200°C. Typically, this region of the lead-tin system exhibits much the same characteristics as the previously discussed 97.5 Pb/2.5 Ag eutectic alloy including poorer wettability than PbSn eutectic and good electrical characteristics (19.5 microhm-cm for the 95 Pb/5 Sn alloy). This system is presently commercially plated in the PCB industry, a distinct advantage. The expected intermetallic compounds on soldering include $AuPb_2$, AuSn, $AuSn_2$, $AuSn_4$, Cu_4Sn, Cu_3Sn, Cu_6Sn_5, $FeSn_2$ and Ni_3Sn_4 and possibly FeSn, CoSn and $CoSn_2$.

Summary – From an analysis of the data the five lead rich systems listed below were selected for Task I of this study. (The Pb-Bi is expected to exhibit poor wettability and in addition the lack of plating history for Bi detracts from its further consideration.) These five systems appear very promising. However, each exhibited certain disadvantages that were recognized and addressed during the course of the study, including: PbAg – corrosion; PbCd – wettability and intermetallic compounds; PbIn – high cost (In); PbSb – questionable wettability; PbSn – Intermetallic formation.

Cadmium Rich Alloys

Three cadmium-rich solder families were available for this study. Binary phase diagrams are shown in views a, b, and c of Figure 2-4 with desired compositional ranges shaded on each diagram. Although Cd is toxic, its alloys were considered for this program due to the attractive characteristics they exhibit.

CdPb – As discussed in the previous topic (Pb-rich alloys), the cadmium-lead phase diagram exhibits a very broad eutectic region, with the eutectic composition appearing on the lead-rich side (see view a). The cadmium-rich side of the diagram is all hyproeutectic with a solidus temperature of 248°C and a liquidus ranging from 275°C at 50% Cd to 315°C at approximately 92% Cd. The cadmium-rich portion of the system should possess approximately the same general characteristics as the lead-rich alloys discussed previously. These include excellent plating capability, potentially good strength, and the same possible intermetallics formed. Electrical resistivity of these alloys is expected to be somewhat lower than those of the lead rich alloys since elemental cadmium exhibits a lower value than elemental lead.

CdSb – The cadmium-antimony system exhibits an eutectic at approximately 9% Sb and 285°C in the temperature range indicated in view b. There is an apparent intermetallic formed (Cd_3Sb_2); however, later data indicates this compound dissociates below 250°C. All compositions within this range have the same solidus temperature while the liquidus temperature increases to 315°C at approximately 3% Sb and approximately 12% Sb on the hypoeutectic and hypereutectic, respectively. The relatively high solidus temperature shows promise for good strength in the 200°C region. Little physical property data is available for this system. For PCB application, both elements can be plated, Sb being less developed. Intermetallic compounds expected from soldering operations include $AuCd_3$, $CuCd_3$, $AuSb_2$ and possibly Cu_5Cd_8, $NiSb_2$ and $CoSb_3$.

CdZn – The cadmium-zinc binary diagram has an eutectic composition of 17.4 Zn at 266°C (see view c). This system has a broad range of alloys available which encompass compositions from approximately 2 Zn to approximately 38 Zn. At 2 Zn, the liquidus is 315°C and the solidus is 300°C

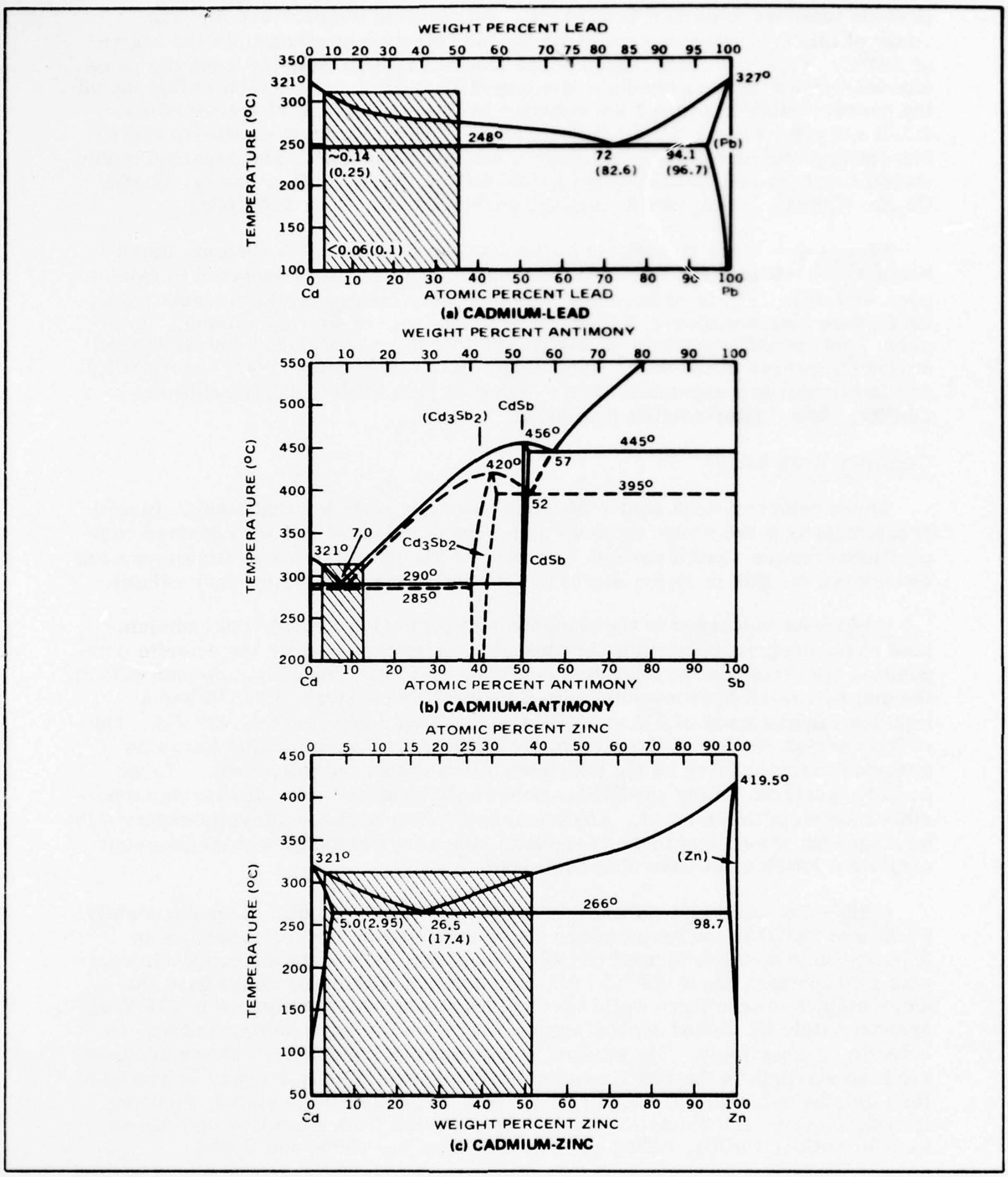

Figure 4. Phase Diagrams for Cadmium Systems CdPb, CdSb and CdZn

which decreases rapidly to the eutectic temperature (266°C) at 5 Sb. At this point, the liquidus is approximately 310°C. The liquidus temperature for the hypereutectic increases to 315°C at 38 Zn. Cadmium-zinc solders are presently available for soldering aluminum assemblies. From this, it is apparent that they will successfully wet copper and gold provided the proper fluxing action is achieved. Little other property data is available. Both elements can be plated, thus provide ease in PCB fabrication. Expected intermetallic compounds include $AuCd_3$, $CuDd_3$, $AuZn_8$, $NiZn_2$, and $NiZn_8$ and possibly Cu_3Cd_8 and $AuZn_3$.

Summary – Due to the relatively high melting points and the relatively simple metallurgy they exhibit, the cadmium rich alloys Cd-Pb, Cd-Sb and Cd-Zn were selected for Task I of this study.

SUMMARY OF ALLOYS SELECTED FOR EVALUATION

From an analysis of the data shown, as well as phase diagrams, and other general information, where available, nine alloy families and one pure metal were selected for inclusion in Task I. See Table 2.

TABLE 2. TASK I CANDIDATE ALLOY LIST

Metal	Compositions	Melting Range °C
Tin	100	232
SnSb	99 Sn	231-235
	90 Sn	246-260
	82 Sn	246-315
PbAg	97.5 Pb	304
PbCd	83 Pb	248
	97 Pb	270-315
PbIn	60 Pb	220-240
	80 Pb	270-280
	94 Pb	310-315
PbSb	82 Pb	252-315
	89 Pb	252
	98 Pb	300-315
PbSn	84 Pb	220-280
	90 Pb	275-300
	96 Pb	310-315
CdPb	50 Cd	248-275
	92 Cd	248-315
CdSb	97 Cd	285-315
	91 Cd	285
	88 Cd	285-315
CdZn	62 Cd	266-315
	83 Cd	266
	98 Cd	300-315

RAW MATERIAL INSPECTION

A sample of each metallic element was gathered and submitted for quantitative chemical spectrographic analysis prior to alloy preparation to determine the purity level of each alloying element. These results are listed in Table 3 and are well within the standard ACS reagent grade requirements.

TABLE 3. RAW MATERIAL QUANTITATIVE CHEMICAL TEST RESULTS

Alloying Metallic Element	Contaminating Elements – Weight Percent								
	Ag	Cu	Fe	Ni	Pb	Bi	Al	Mg	Ca
Antimony	0.01	0.00007	0.003	0.0008	0.04	T	T	T	T
Cadmium	0.0002	0.0005	T	T	0.0009	0.0009	T	T	T
Lead	T	T	T	T	T	T	T	T	T
Tin	T	0.00003	0.0002	0.0001	T	0.00006	T	T	T
Zinc	0.0001	0.0002	T	T	0.0003	T	T	T	T
Indium	T	T	0.0002	0.00002	0.0004	T	0.0002	0.0001	0.00002

T = Trace ($< 5 \times 10^{-6}$)

ALLOY PREPARATION

Six different metallic elements were utilized for preparing the proposed candidate alloys. A master melt of each candidate alloy was prepared from which a 2-1/2 x 3 x 1/8 inch ingot blank (15 milliliter volume), 15 milliliter cylindrical ingot and 10 milliliter plug were cast. The ingot blank was rolled into sheet stock which was subsequently used for solderability preforms and coupons for the electrical resistivity determination. The cylindrical ingot was remelted for purposes of solder dip application. The random shaped plug was used as the test sample for the wet chemical analysis.

The desired weight percentages for each metallic element were prepared for each candidate solder alloy and placed in a 50 milliliter crucible. Utilizing an induction unit as the heat source and a glove box containing the induction coil, the solder alloys were prepared in a dry inert (argon) atmosphere.

COOLING CURVE DETERMINATION

After each master melt had been thoroughly mixed and held approximately 150°C above the freezing point of the alloy, the molten metal was allowed to cool. The resulting cooling rate was monitored with a standard chart driven recording device. A typical cooling curve derived from one of the candidate alloys is illustrated in Figure 5. Solidus and liquidus temperatures for each of the candidate alloys were determined. The results are listed in Table 4.

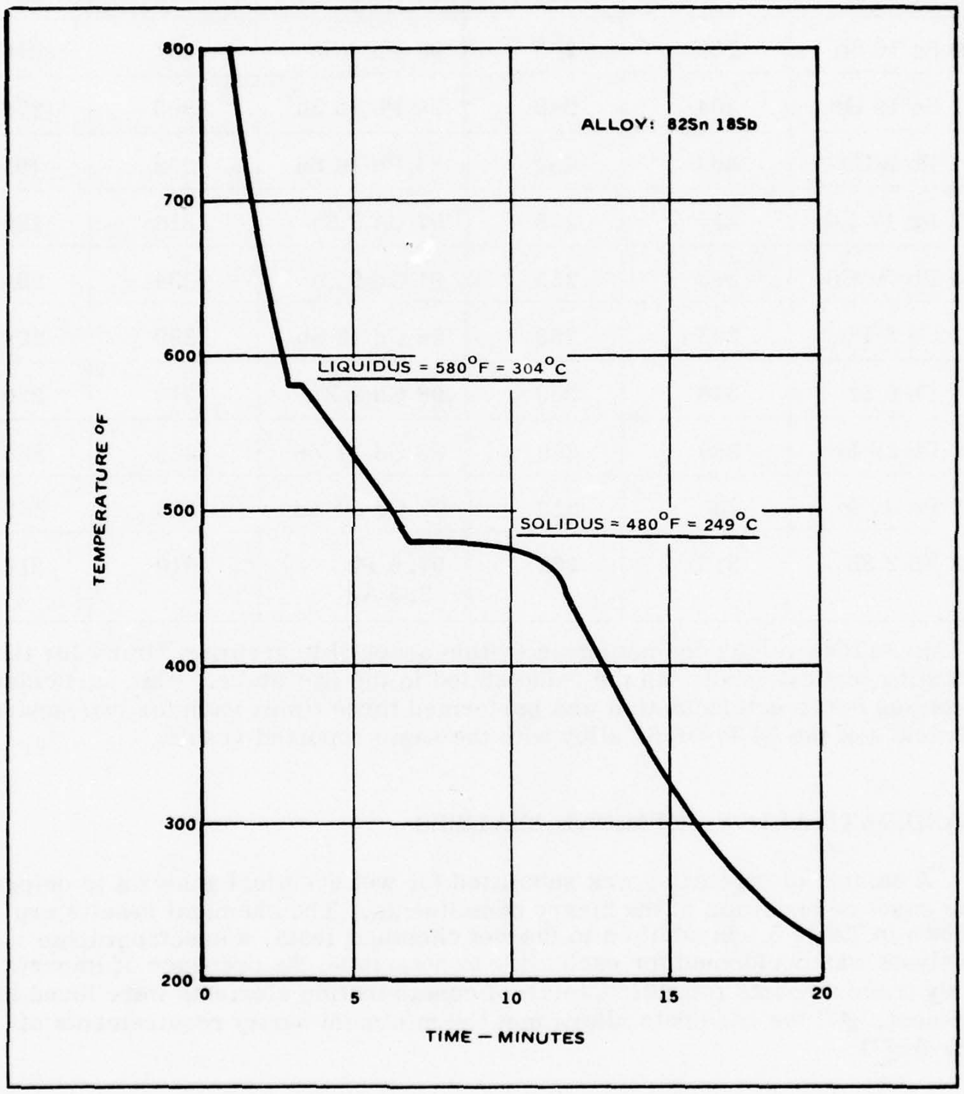

Figure 5. Typical Cooling Curve

TABLE 4. SOLDER ALLOY SOLIDUS AND LIQUIDUS TEMPERATURE DETERMINATION RESULTS

Alloy	Liquidus Temp °C	Solidus Temp °C	Alloy	Liquidus Temp °C	Solidus Temp °C
100 Sn	240	240	89 Pb 11 Sb	252	252
99 Sn 1 Sb	246	235	82 Pb 18 Sb	315	257
90 Sn 10 Sb	259	249	96 Pb 4 Sn	321	310
82 Sn 18 Sb	304	249	90 Pb 10 Sn	305	278
97 Pb 3 Cd	304	250	84 Pb 16 Sn	292	191*
83 Pb 17 Cd	255	255	97 Cd 3 Sb	316	296
50 Pb 50 Cd	283	255	91 Cd 9 Sb	294	294
92 Cd 8 Pb	305	253	88 Cd 12 Sb	299	294
94 Pb 6 In	318	309	98 Cd 2 Zn	318	290
80 Pb 20 In	280	260	83 Cd 17 Zn	268	268
60 Pb 40 In	233	213	62 Cd 38 Zn	313	269
98 Pb 2 Sb	315	302	97.5 Pb 2.5 Ag	310	310

*This solidus value does not agree (within acceptable accuracy limits for the testing method used) with the value stated in the literature. This particular cooling curve determination was performed three times each for two separate batches of the 84 Pb 16 Sn alloy with the same reported result.

CANDIDATE ALLOY CHEMICAL ANALYSIS

A sample of each alloy was submitted for wet chemical analysis to determine the exact composition of the binary constituents. The chemical results are shown in Table 5. In addition to the wet chemical tests, a spectrographic analysis was performed for each alloy to determine the presence of impurities. Only trace amounts (<0.0015% total) of contaminating elements were found to be present. All the candidate alloys met the minimum purity requirements of QQ-S-571.

TABLE 5. SOLDER ALLOY QUANTITATIVE CHEMICAL TEST RESULTS

Alloy	Metallic Element - Wt %					Alloy	Metallic Element - Wt %					
	Sn	Pb	Cd	Sb	In		Ag	Sn	Pb	Cd	Zn	Sb
100 Sn	100	--	--	--	--	89Pb11Sb	--	--	bal	--	--	11.0
99Sn1Sb	bal	--	--	1.24	--	82Pb18Sb	--	--	bal	--	--	17.2
90Sn10Sb	bal	--	--	9.85	--	96Pb4Sn	--	4.08	bal	--	--	--
82Sn18Sb	bal	--	--	17.4	--	90Pb10Sn	--	10.2	bal	--	--	--
97Pb3Cd	--	bal	3.10	--	--	84Pb16Sn	--	16.2	bal	--	--	--
83Pb17Cd	--	bal	16.8	--	--	97Cd3Sb	--	--	--	bal	--	2.85
50Pb50Cd	--	bal	49.5	--	--	91Cd9Sb	--	--	--	bal	--	9.0
92Cd8Pb	--	8.72	bal	--	--	88Cd12Sb	--	--	--	bal	--	12.0
94Pb6In	--	bal	--	--	6.1	98Cd2Zn	--	--	--	bal	2.12	--
80Pb20In	--	bal	--	--	20.4	83Cd17Zn	--	--	--	bal	17.0	--
60Pb40In	--	bal	--	--	40.0	62Cd38Zn	--	--	--	bal	39.5	--
98Pb2Sb	--	bal	--	2.09	--	97.5Pb 2.5Ag	2.43	--	bal	--	--	--

SOLDERABILITY TEST CONFIGURATION AND PROCEDURE

The 2-1/2 x 3 x 1/8 inch blank that was cast of each candidate alloy was subsequently rolled, through a standard mill, into 3 by 0.015 inch strip material. Circular disks, one half inch in diameter, were made from the strips for each solder alloy and were used as the standard preform configuration for the solderability test.

The solderability of each candidate alloy was determined on copper, bare Kovar and gold plated Kovar surfaces. The base metal samples were sheared into one inch squares and thoroughly cleaned just prior to soldering.

Solderability test samples were placed inside a glove box continuously purged with specially dried argon gas. The base sheet metal pieces were placed on a contained hot plate that was maintained at 25 to 35^{o}C above the melting temperature of the particular solder alloy being tested. The individual preforms for each candidate alloy were immersed in liquid flux (Type RMA per MIL-F-14256) prior to melting and allowed to melt and spread over copper, Kovar and gold plated Kovar surfaces for a period of one minute.

SOLDERABILITY SPREAD RATING RESULTS

The degree of spread of the candidate alloys over each base material test surface was graded using the standard alloy as a basis of comparison. Each combination was rated as better than (B), equal to (E) or less than (L) the standard alloy. These results are shown in Table 6.

TABLE 6. CANDIDATE ALLOY SOLDERABILITY SPREAD RATING RESULTS USING Sn63 AS A COMPARATIVE STANDARD

	Base Material				Base Material		
Alloy	Au-Plated Kovar	Kovar	Copper	Alloy	Au-Plated Kovar	Kovar	Copper
100Sn	E	E	E	89Pb11Sb	L	L	L
99Sn1Sb	L	E	L	82Pb18Sb	L	L	L
90Sn10Sb	L	E	L	96Pb4Sn	E	E	L
82Sn18Sb	L	E	L	90Pb10Sn	L	L	L
97Pb3Cd	L	L	L	84Pb16Sn	L	E	L
83Pb17Cd	L	L	L	97Cd3Sb	L	L	B
50Pb50Cd	L	L	E	91Cd9Sb	L	L	B
92Cd8Pb	E	L	E	88Cd12Sb	L	L	B
94Pb6In	L	E	L	98Cd2Zn	L	L	B
80Pb20In	L	L	L	83Cd17Zn	L	L	E
60Pb40In	E	L	L	62Cd38Zn	L	E	L
98Pb2Sb	L	L	L	97.5Pb2.5Ag	E	L	L

The solderability test samples for Sn63 standard alloy and the candidate alloys are shown in Figures 6 through 30.

Figure 6. Solder Alloy – Sn63

Figure 7. Solder Alloy – 100 Sn

Figure 8. Solder Alloy – 97.5Pb 2.5Ag

Figure 9. Solder Alloy – 92Cd 8Pb

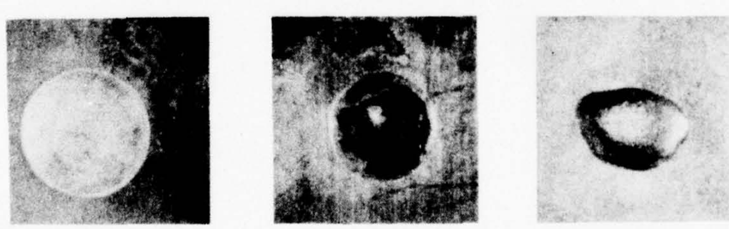

Figure 10. Solder Alloy – 99Sn 1Sb

Figure 11. Solder Alloy – 90Sn 10Sb

Figure 12. Solder Alloy – 82Sn 18Sb

Figure 13. Solder Alloy – 97Pb 3Cd

Figure 14. Solder Alloy – 83Pb 17Cd

Figure 15. Solder Alloy – 50Pb 50Cd

Figure 16. Solder Alloy – 94Pb 6In

Figure 17. Solder Alloy – 80Pb 20In

Figure 18. Solder Alloy – 60Pb 40In

AU-PLATED KOVAR | KOVAR | COPPER

Figure 19. Solder Alloy – 98Pb 2Sb

AU-PLATED KOVAR | KOVAR | COPPER

Figure 20. Solder Alloy – 89Pb 11Sb

AU-PLATED KOVAR | KOVAR | COPPER

Figure 21. Solder Alloy – 82Pb 18Sb

AU-PLATED KOVAR | KOVAR | COPPER

Figure 22. Solder Alloy – 96Pb 4Sn

Figure 23. Solder Alloy – 90Pb 10Sn

Figure 24. Solder Alloy – 84Pb 16Sn

Figure 25. Solder Alloy – 97Cd 3Sb

Figure 26. Solder Alloy – 91Cd 9Sb

Figure 27. Solder Alloy – 88Cd 12Sb

Figure 28. Solder Alloy – 98Cd 2Zn

Figure 29. Solder Alloy – 83Cd 17Zn

Figure 30. Solder Alloy – 62Cd 38Zn

In addition to rating each alloys wetting characteristics with respect to the standard Sn63, it was also important to rate them with respect to each other. A number grading system was used ranging from 0 to 5 with the highest number indicating the best degree of wetting. A verbal description of the ratings used in the alloy summary is:

0 = No wetting
1 = Poor
2 = Fair
3 = Average
4 = Good
5 = Excellent

The results are listed in Table 7 along with a total overall rating.

TABLE 7. OVERALL CANDIDATE ALLOY SOLDERABILITY SPREAD RATING RESULTS

Alloy	Base Material			Total Rating	Alloy	Base Material			Total Rating
	Au-Plated Kovar	Kovar	Copper			Au-Plated Kovar	Kovar	Copper	
Sn63	5	4	4	13	89Pb11Sb	3	2	1	6
100Sn	5	4	4	13	82Pb18Sb	4	3	1	8
99Sn1Sb	3	4	2	9	96Pb4Sn	4	3	3	10
90Sn10Sb	4	4	2	10	90Pb10Sn	4	1	3	8
82Sn18Sb	4	3	2	9	84Pb16Sn	3	4	3	10
97Pb3Cd	3	1	3	7	97Cd3Sb	4	2	5	11
83Pb17Cd	3	3	3	9	91Cd9Sb	3	3	5	11
50Pb50Cd	3	3	4	10	88Cd12Sb	3	1	5	9
92Cd8Pb	5	3	4	12	98Cd2Zn	2	2	5	9
94Pb6In	4	4	3	11	83Cd17Zn	2	1	3	6
80Pb20In	3	1	3	7	62Cd38Zn	2	4	3	9
60Pb40In	4	3	3	10	97.5 Pb 2.5 Ag	5	0	2	7
98Pb2Sb	3	2	0	5					

ELECTRICAL RESISTIVITY TEST CONFIGURATION AND PROCEDURE

Since the literature offered no electrical resistivity values for the particular candidate alloys of this program and electrical resistivity properties are considered an essential part of the alloy screening phase of Task I, the actual resistivity for each alloy was determined experimentally. Resistivity measurements were made on specimens 0.476 cm wide, 20 cm long and 0.038 cm thick using a four terminal Kelvin Bridge. The results are listed in Table 8.

TABLE 8. CANDIDATE ALLOY ELECTRICAL RESISTIVITY DETERMINATION RESULTS

Alloy	Resistivity ohm-cm x 10^{-6}	Alloy	Resistivity ohm-cm x 10^{-6}	Alloy	Resistivity ohm-cm x 10^{-6}
Sn63	14.73*	92Cd8Pb	7.25	90Pb10Sn	20.30
100Sn	12.85**	94Pb6In	29.18	84Pb16Sn	19.49
99Sn1Sb	15.06	80Pb20In	36.09	97Cd3Sb	9.03
90Sn10Sb	16.95	60Pb40In	33.40	91Cd9Sb	10.99
82Sn18Sb	19.77	98Pb2Sb	23.06	88Cd12Sb	12.72
97Pb3Cd	19.69	89Pb11Sb	25.47	98Cd2Zn	7.53
83Pb17Cd	17.16	82Pb18Sb	30.08	83Cd17Zn	7.60
50Pb50Cd	11.26	96Pb4Sn	22.59	62Cd38Zn	7.31
				97.5 Pb-2.5Ag	20.58

*The resistivity value reported in the literature for this particular alloy is 13.47 x 10^{-6} ohm-cm. Since resistivity is also directly proportional to the amount of induced cold work, the reported values are expected to be slightly higher than literature values.

**The electrical resistivity values in the literature for the pure metallic elements used are as follows: Sb – 41.7 x 10^{-6} (20°C); In – 8.37 x 10^{-6} (0°C); Sn – 11.5 x 10^{-6} (20°C); Ag – 1.63 x 10^{-6} (18°C); Cd – 7.54 x 10^{-6} (18°C); Pb – 22.0 x 10^{-6} (20°C); Zn – 5.75 x 10^{-6} (0°C)

45° BOND STRENGTH TEST CONFIGURATION AND PROCEDURE

Samples for the 45 degree pull test were soldered using solder-coated, gold-plated Kovar leads. A Hughes MCW/EL capacitor discharge welding machine was used in conjunction with a DC power supply and a peg type resistance heater tip. The joint was made by reflow soldering the previously solder-coated lead to the previously solder-coated, copper clad, polyimide board material using type RMA flux per MIL-F-14256. This fluxing operation reduces any oxides that may exist prior to or form during the soldering process thereby increasing the bond strength of the joint. Figure 31 illustrates a typical lead-to-board solder joint.

Figure 31. X-14 Photomacrograph of a Typical Lead-to-Board Solder Joint. The previously solder-coated lead and board material have been reflow soldered forming a fillet around the edges of the ribbon lead wire.

ROOM TEMPERATURE AND ELEVATED TEMPERATURE BOND STRENGTH RESULTS

Samples for the 45 degree pull test were prepared and tested at room temperature and 200°C. Figure 32 illustrates the test set-up used for these ambient and elevated temperature tests. Ten individual pull tests were performed for each solder alloy and test temperature combination. Table 9 lists the room temperature and elevated temperature average bond strength values for each candidate alloy. General conclusions drawn from the data shown in Table 9 are as follows:

a. Where lead is one of the alloying binary constituents, the bond strength increases with increased lead content.

b. Solder alloys containing antimony seem to produce more brittle solder joints particularly in the copper clad material during exposure to elevated temperature.

c. The cadmium-zinc solder alloys experience a significant decrease in bond strength properties during high temperature exposure.

d. Where indium is one of the alloying binary constituents, the elevated temperature bond strength properties decrease with increased indium content.

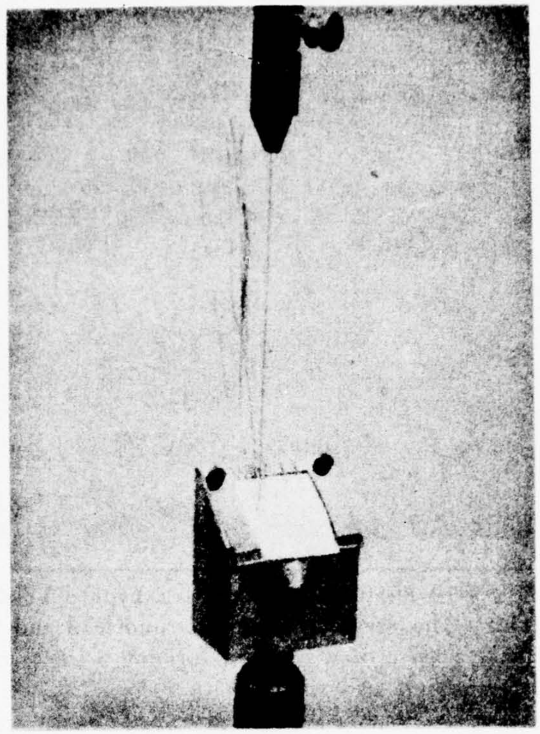

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Figure 32. The 45-Degree Bond Strength Peel Test Set-Up. The fixture was also used in conjunction with a Missimers furnace for the elevated temperature tests.

TABLE 9. ROOM TEMPERATURE AND ELEVATED TEMPERATURE AVERAGE 45° BOND STRENGTH RESULTS (LBS)

Solder Alloy	Testing Temp**		20°C*** Failure Mode	200°C Failure Mode	Solder Alloy	Testing Temp		20°C Failure Mode	200°C Failure Mode
	20°C	200°C				20°C	200°C		
Sn63*	0.55	0.24	LS	LS	60Pb40In	0.85	0.02	LS	LS
100Sn	0.85	0.24	LS	LS	96Pb4Sn	1.42	0.65	LS	LS
99Sn1Sb	0.69	0.12	LS	LS	90Pb10Sn	1.18	0.60	LS	LS
90Sn10Sb	0.35	0.29	LS	LS&C	84Pb16Sn	1.27	0.28	LS	LS
82Sn18Sb	0.45	0.39	LS	C	97Cd3Sb	1.01	0.61	LS	LS&C
97Pb3Cd	1.09	0.97	LS	LS&C	91Cd9Sb	0.92	0.39	LS&C	LS
83Pb17Cd	0.92	1.00	LS	LS	88Cd12Sb	0.77	0.91	LS	C
50Pb50Cd	0.67	0.34	LS	LS	98Cd2Zn	2.10	0.21	LS	LS
92Cd9Pb	0.94	0.31	LS	LS	83Cd17Zn	1.46	0.53	LS	LS
94Pb6In	0.67	0.49	LS	LS	62Cd38Zn	1.05	0.00	LS	LS
80Pb20In	1.17	0.27	LS	LS					

*Sn63 – Samples were tested at 125°C

**The strength values reported are based upon a 0.017 inch lead width

***LS – Lead to solder failure; C – Copper cladding to board failure

METALLURGICAL COMPATIBILITY STUDY

Each base material (gold plated Kovar and copper) and solder alloy combination was tested to determine the intermetallic compound growth rate experienced during soldering and high temperature exposure (200°C for 200 hours). Scanning electron microscope (SEM) line scans were made across sectioned soldered interfaces for the "as soldered" and "as exposed" conditions. In this manner, the amount of intermetallic compound formed during high temperature exposure was monitored. These line scans were also used for purposes of identifying the intermetallic compound products by determining their approximate (±10%) chemical composition. In addition to the SEM analysis, the samples were examined optically to establish the structural integrity of the joints. The metallurgical compatibility data derived from the SEM line scans and optical analyses are shown in Table 10.

CANDIDATE ALLOY SUMMARY

In order for each candidate alloy to be effectively evaluated, it is necessary to itemize the alloy characterization test results and conclusions for each solder alloy. In this manner, an individual overall performance rating can be established. Since several alloys failed to adequately wet a copper surface during the solderability test, they were immediately screened from the original candidate alloy list. Therefore, subsequent characterization testing was suspended for these alloys and is so noted in the summary format by the inclusion of NTP (no test performed) in the appropriate property column.

<u>Solder Alloy: 100 Sn</u>

Liquidus Temperature	240°C
Solidus Temperature	240°C
Solderability Rating	
A. Copper Surface:	Good
B. Au-Plated Kovar Surface:	Excellent
C. Kovar Surface:	Good
Electrical Resistivity (x10^{-6} ohm-cm):	12.85
Average 45° Bond Strength (lbs)	
A. Room Temperature	0.85
B. Elevated Temperature (200°C)	0.34

TABLE 10. METALLURGICAL CO

SOLDER ALLOY	PHASES FORMED ON COPPER SURFACE					PHASES FORMED	
	AS SOLDERED CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.	200°C FOR 200 HOURS CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.	NET CHANGE IN THICKNESS $\times 10^{-4}$ IN.	AS SOLDERED CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.
100Sn	None	-	Cu_3Sn	0.95	5.8	None	-
			Cu_6Sn_5	4.85			
99Sn1Sb	None	-	Cu_3Sn	1.0	6.0	None	-
			Cu_6Sn_5	5.0			
90Sn10Sb	Cu_6Sn_5	(See Rem. #1) 10.0 (Total)	Cu_6Sn_5	(See Rem. #1) 15.0 (Total)	5.0	None	-
82Sn18Sb	None	-	Cu_6Sn_5	4.0	4.0	None	-
97Pb3Cd	None	-	Cu_5Cd_8	3.7	3.7	None	-
83Pb17Cd	None	-	$CuCd_3$	9.5	9.5	$AuCd_3$	9.5
50Pb50Cd	None	-	$CuCd_3$	8.0	8.0	$AuCd_3$	0.83
92Cd8Pb	None	-	$CuCd_3$	11.7	11.7	None	-
94Pb6In	In	0.63	None	-	-	None	-
80Pb20In	In	0.70	Cu_9In_7	3.8	3.8	$AuIn_2$	7.5

10. METALLURGICAL COMPATIBILITY RESULTS

NET CHANGE IN THICKNESS X 10^{-4} IN.	PHASES FORMED ON GOLD PLATED KOVAR SURFACE					REMARKS
	AS SOLDERED CONDITION	PHASE THICKNESS X 10^{-4} IN.	200°C FOR 200 HOURS CONDITION	PHASE THICKNESS X 10^{-4} IN.	NET CHANGE IN THICKNESS X 10^{-4} IN.	
5.8	None	-	(See Rem. #2) $AuSn_4$	14.0	14.0	1. The tin-gold intermetallic compound was in needle form prior to exposure and in layer form following high temperature exposure. 2. The $AuSn_4$ layer is tin rich (mixed with solder).
6.0	None	-	(See Rem. #2) $AuSn_4$	2.5	2.5	1. The tin-gold intermetallic compound needles were dissolved during high temperature exposure. 2. $AuSn_4$ phase is mixed with solder (tin rich).
5.0	None	-	(See Rem. #2) $AuSn_4$	3.1	3.1	1. The deposition of the Cu_6Sn_5 intermetallic compound at the copper interface is in granular form (particles of Cu_6Sn_5 mixed with solder). 2. The tin-gold intermetallic compound occurred in needle form following soldering and was redeposited in layer form during the high temperature exposure ($AuSn_4$ mixed with solder).
4.0	None	-	(See Rem. #2) $AuSn_4$	0.83	0.83	1. The tin-gold intermetallic compound needles were dissolved during high temperature exposure. 2. The $AuSn_4$ phase is mixed with solder (tin rich).
3.7	None	-	None	-	-	1. Cadmium-gold intermetallic compound phase is present in particle form prior to and following high temperature exposure.
9.5	$AuCd_3$	9.5	$AuCd_3$	3.0	-6.5	1. The $AuCd_3$ intermetallic compound layer was lifted from the Kovar surface but remained in layer form. 2. Most of the $AuCd_3$ phase was dissolved during high temperature exposure.
8.0	$AuCd_3$	0.83	$AuCd_3$	0.83	0	1. Gold-plated Kovar interface crack detected prior to exposure. 2. This interface cracking was enlarged during exposure.
11.7	None	-	None	-	-	1. Gold-plated Kovar interface crack indication formed during exposure. 2. Cadmium-gold intermetallic compound phase remained in particle form following exposure
-	None	-	None	-	-	1. Indium migrated to the copper surface during the soldering operation. 2. Indium and lead formed solid solutions with copper during high temperature exposure. 3. The indium-gold intermetallic compound remained in particle form following high temperature exposure.
3.8	$AuIn_2$	7.5	$AuIn_2$	5.0	-2.5	1. Pure indium migrated to the copper interface during soldering. 2. Lead contamination within the $AuIn_2$ intermetallic compound layer has occurred during soldering. 3. Delamination of the $AuIn_2$ layer has occurred in a lead rich zone during high temperature exposure.

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TABLE 10. METALLURGICAL COMPATIBILITY RESU

SOLDER ALLOY	PHASES FORMED ON COPPER SURFACE: AS SOLDERED CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.	200°C FOR 200 HOURS CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.	NET CHANGE IN THICKNESS $\times 10^{-4}$ IN.	PHASES FORMED ON GOLD PLATED KOVAR SU: AS SOLDERED CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.	200°C FOR 200 HOURS CONDITION	PHAS THICKN $\times 10^{-4}$
60Pb40In	In	1.30	Cu_9In_7	1.5	5.0	None	-	None	-
			Cu_9In_4	2.0					
			Cu_9In_7	1.5					
96Pb4Sn	None	-	Cu_3Sn	5.0	12.5	None	-	None	-
			Cu_6Sn_5	7.5					
90Pb10Sn	None	-	Cu_3Sn	3.30	4.10	Sn in Fe	1.3	Sn in Fe	1.3
			Cu_6Sn_5	0.80					
84Pb16Sn	None	-	Cu_3Sn	2.8	17.8	Sn in Fe	1.2	Sn in Fe	3.1
			Cu_6Sn_5	15.0					
97Cd3Sb	None	-	Cu_5Cd_8	5.0	10.0	None	-	None	-
			$CuCd_3$	5.0					
91Cd9Sb	$CuCd_3$	3.1	Cu_5Cd_8	5.6	5.0	None	-	None	-
			$CuCd_3$	2.5					
88Cd12Sb	$CuCd_3$	1.9	Cu_5Cd_8	5.0	5.0	None	-	None	-
			$CuCd_3$	2.8	0.9				
98Cd2Zn	None	-	$Cu_3Cd_3Zn_4$	2.2	2.2	Zn	0.60	Zn	0.9
83Cd17Zn	Zn	0.94	$Cu_3Cd_3Zn_4$	12.5	12.5	None	-	-	Non
62Cd38Zn	Zn	1.3	$Cu_3Cd_3Zn_4$	16.0	14.7	$AuZn_8$	5.6	$AuZn_8$	5.0
	$Cu_3Cd_3Zn_4$	1.3							

LURGICAL COMPATIBILITY RESULTS(Continued)

	PHASES FORMED ON GOLD PLATED KOVAR SURFACE				
S ERED ITION	PHASE THICKNESS $\times 10^{-4}$ IN.	200°C FOR 200 HOURS CONDITION	PHASE THICKNESS $\times 10^{-4}$ IN.	NET CHANGE IN THICKNESS $\times 10^{-4}$ IN.	REMARKS
ne	-	None	-	-	1. The indium-gold intermetallic compound remained in particle form following high temperature exposure. 2. Crack indication at the gold-plated Kovar interface was detected prior to exposure.
ne	-	None	-	-	1. Pure lead, from the solder alloy, is mixed with the Cu_6Sn_5 intermetallic compound layer 2. The tin-gold intermetallic compound is in particle form prior to and following exposure.
in Fe	1.3	Sn in Fe	1.3	0	1. The tin-gold intermetallic compound is in particle form prior to and following high temperature exposure. 2. After the tin-gold intermetallic compound was lifted from the Kovar surface, the tin formed a solid solution with the iron constituent.
in Fe	1.2	Sn in Fe	3.1	1.9	1. The tin-gold intermetallic compound is in particle form prior to and following exposure. 2. After the tin-gold intermetallic compound was lifted from the Kovar surface, the tin formed a solid solution with the iron constituent.
None	-	None	-	-	1. Crack indication present at the copper interface prior to and following exposure. 2. The cadmium-gold intermetallic compound has completely dissolved in the cadmium rich solder during the soldering operation.
None	-	None	-	-	1. Crack indications are present at the copper interface prior to and following high temperature exposure. 2. The cadmium-gold intermetallic compound was completely dissolved by the cadmium rich solder alloy during soldering.
None	-	None	-	-	1. The cadmium-gold intermetallic compound was completely dissolved during the soldering operation. 2. Crack indications are present at the copper interface prior to and following exposure.
Zn	0.60	Zn	0.94	0.34	1. Because of the formation of the ternary intermetallic compound on the copper surface, the solder alloy adjacent to the solder interface was completely depleted of zinc. 2. The gold intermetallic compound was completely dissolved by the cadmium rich solder alloy.
None	-	-	None	-	1. Because of the formation of the ternary intermetallic compound on the copper surface, the solder alloy adjacent to the solder interface was completely depleted of zinc. 2. The zinc-gold intermetallic compound remained in particle form following exposure.
$AuZn_8$	5.6	$AuZn_8$	5.0	-0.6	1. Due to the formation of the ternary intermetallic compound on the copper surface, the solder alloy adjacent to the solder interface was completely void of zinc content. 2. The zinc-gold intermetallic compound remained in layer form following exposure.

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Metallurgical Compatibility

A. Copper Base Material: Fair

B. Au-Plated Kovar Base Material: Poor

Comments and Conclusions

1. Following high temperature exposure, the $AuSn_4$ intermetallic compound was apparently redeposited on the Kovar surface in layer form through a tin-gold eutectic reaction. This type of redeposition is considered to be unsuitable for high temperature type applications.

2. The intermetallic compound reaction on the copper surface is a two stage process; first, the copper reacts with the tin to form the copper rich Cu_3Sn phase; secondly, the Cu_3Sn reacts with the excess tin in the solder alloy to form the Cu_6Sn_5 phase (see Table 10).

Solder Alloy: 99Sn1Sb

Liquidus Temperature: $246^{\circ}C$

Solidus Temperature: $235^{\circ}C$

Solderability Rating

A. Copper Surface: Fair

B. Au-Plated Kovar Surface: Average

C. Kovar Surface: Good

Electrical Resistivity ($x10^{-6}$ ohm-cm): 15.06

Average 45° Bond Strength (lbs)

A. Room Temperature: 0.69

B. Elevated Temperature ($200^{\circ}C$) 0.12

Metallurgical Compatibility

A. Copper Base Material: Fair

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. The antimony content of the solder alloy seemed to significantly reduce the $AuSn_4$ redeposition rate experienced by the 100Sn alloy.

2. Due to the redeposition of the $AuSn_4$ phase during high temperature exposure and relatively low elevated temperature bond strength properties, this alloy is considered to be unacceptable for high temperature type applications.

Solder Alloy: 90Sn10Sb

Liquidus Temperature: 259°C

Solidus Temperature: 249°C

Solderability Rating

A. Copper Surface: Fair

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Good

Electrical Resistivity ($x10^{-6}$ ohm-cm): 16.95

Average 45° Bond Strength (lbs)

A. Room Temperature: 0.35

B. Elevated Temperature (200°C): 0.29

Metallurgical Compatibility

A. Copper Base Material: Fair

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. The ten percent addition of antimony retarded the tin-gold eutectic reaction about as much as the one percent addition in the 99Sn1Sb alloy (see Table 10).

2. During solidification of the solder alloy, SbSn intermetallic compound particles form through a peritectic reaction and float to the surface of the molten solder mass. Since these particles are not dispersed uniformly throughout the molten solder, a gravimetric type of segregation occurs which depletes the subsurface solder mass of antimony.

Solder Alloy: 82Sn18Sb

Liquidus Temperature: 304°C

Solidus Temperature: 249°C

Solderability Rating

A. Copper Surface: Fair

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): 19.77

Average 45° Bond Strength (lbs)

A. Room Temperature: 0.45

B. Elevated Temperature (200°C) 0.39

Metallurgical Compatibility

A. Copper Base Material: Fair

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. The eighteen percent addition of antimony further suppressed the tin-gold eutectic reaction thereby minimizing redeposition during high temperature exposure (see Table 10).

2. Since this alloy is richer in antimony content, it is more prone to segregate gravimetrically during solidification.

3. The antimony content has a tendency to cause embrittlement of the copper clad material during high temperature exposure (see the applicable failure mode in Table 9.

Solder Alloy: 97Pb3Cd

Liquidus Temperature: 304°C

Solidus Temperature: 250°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Average

C. Kovar Surface: Poor

Electrical Resistivity ($x10^{-6}$ ohm-cm): 19.69

Average 45° Bond Strength (lbs)

A. Room Temperature: 1.09

B. Elevated Temperature (200°C): 0.97

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. As is expected from a lead rich solder alloy, the room temperature and elevated temperature bond strength properties are excellent.

2. Solderability and electrical resistivity properties are considered to be marginal.

Solder Alloy: 83Pb17Cd

Liquidus Temperature:	255°C
Solidus Temperature:	255°C

Solderability Rating

A. Copper Surface:	Average
B. Au-Plated Kovar Surface:	Average
C. Kovar Surface:	Average
Electrical Resistivity ($x10^{-6}$ ohm-cm):	17.16

Average 45° Bond Strength (lbs)

A. Room Temperature:	0.92
B. Elevated Temperature (200°C):	1.00

Metallurgical Compatibility

A. Copper Base Material:	Fair
B. Au-Plated Kovar Base Material:	Fair

Comments and Conclusions

1. The metallurgical compatibility data indicates the sequence of chemical reactions for this solder alloy on a gold-plated Kovar surface to be as follows (see Table 10):

   a. Formation of the $AuCd_3$ intermetallic compound layer.
   b. Lifting of the $AuCd_3$ layer from the Kovar surface.
   c. Dissolution of the $AuCd_3$ layer into the solder alloy matrix.

2. The increased cadmium content accelerates the copper-cadmium intermetallic compound formation rate. Figure 33 illustrates the chemical gradient from the copper base material across the soldered interface into the solder alloy. This data was transposed from a SEM line scan so that the copper-cadmium intermetallic compound interface reaction can be illustrated in a more readable format (view a). The $CuCd_3$ intermetallic reaction is shown to have progressed to a depth of 0.00095 inches (view b).

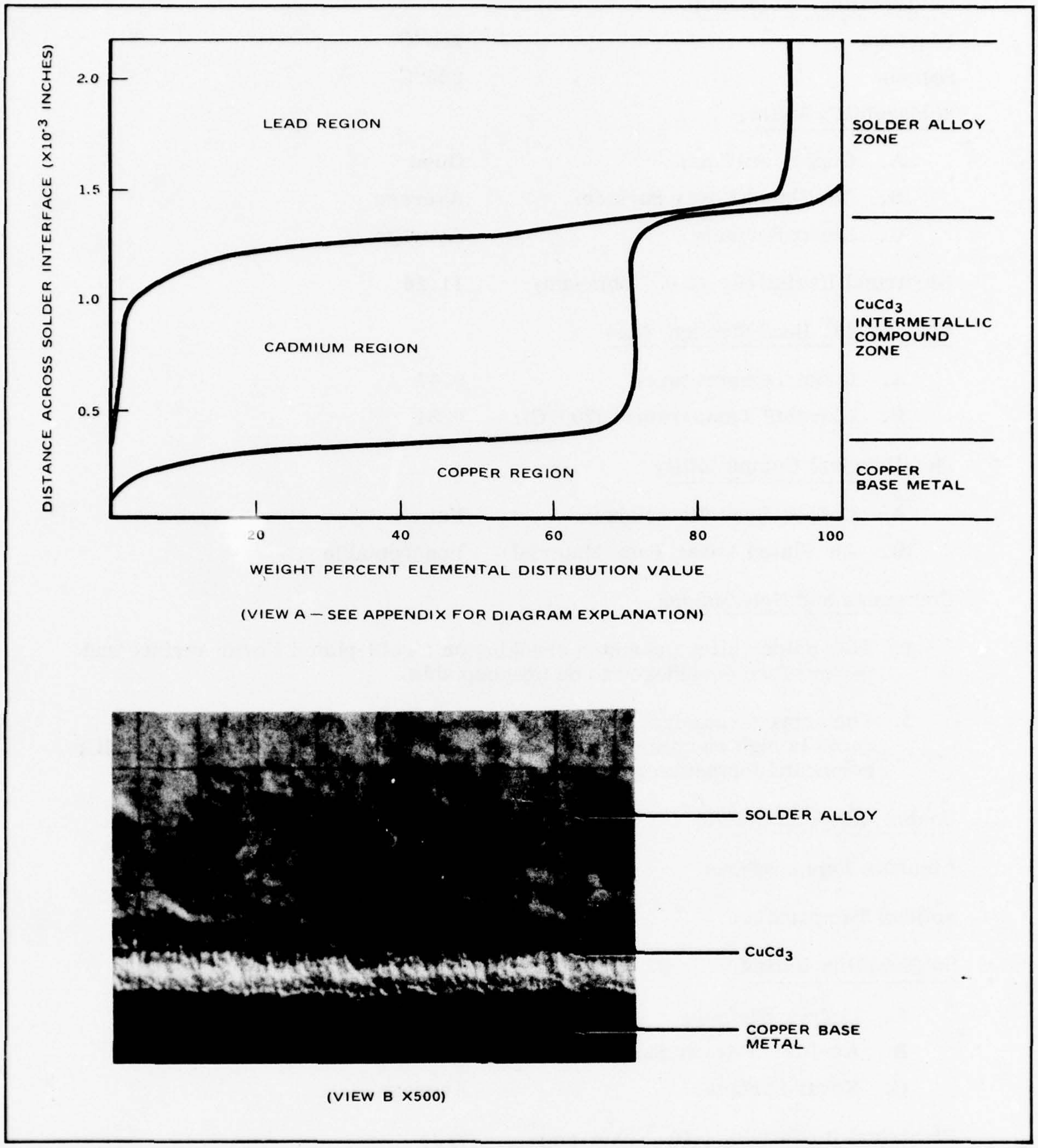


Figure 33. Copper Surface 83 Pb 17 Cd Solder Alloy Interface Reaction (Following Exposure to 200°C for 200 Hours)

Solder Alloy: 50Pb50Cd

Liquidus	283°C
Solidus	255°C

Solderability Rating

A. Copper Surface:	Good
B. Au-Plated Kovar Surface:	Average
C. Kovar Surface:	Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): 11.26

Average 45° Bond Strength (lbs)

A. Room Temperature:	0.67
B. Elevated Temperature (200°C):	0.34

Metallurgical Compatibility

A. Copper Base Material:	Fair
B. Au-Plated Kovar Base Material:	Unacceptable

Comments and Conclusions

1. This solder alloy promotes cracking on a gold-plated Kovar surface and is therefore considered to be unacceptable.

2. The copper-cadmium intermetallic compound formation rate is more rapid in high cadmium content alloys than is the copper-tin intermetallic compound formation rate in high tin content alloys (see Table 10).

Solder Alloy: 92Cd8Pb

Liquidus Temperature:	305°C
Solidus Temperature:	253°C

Solderability Rating

A. Copper Surface:	Good
B. Au-Plated Kovar Surface:	Excellent
C. Kovar Surface:	Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): 7.25

Average 45° Bond Strength (lbs)

A. Room Temperature:	0.94
B. Elevated Temperature (200°C):	0.31

Metallurgical Compatibility

A. Copper Base Material: Poor

B. Au-Plated Kovar Base Material: Unacceptable

Comments and Conclusions

1. Interface cracking was found to occur on the gold-plated Kovar surface during high temperature exposure. It is concluded that high cadmium - low lead solder alloys produce interface cracks on gold-plated surfaces and are therefore considered to be unacceptable.

2. Due to the high cadmium content of this solder alloy, the copper-cadmium intermetallic compound formation rate is extremely rapid (see Table 10).

Solder Alloy: 94Pb6In

Liquidus Temperature: 318°C

Solidus Temperature: 309°C

Solderability Rating

A. Copper Surface: Fair

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Good

Electrical Resistivity ($x10^{-6}$ ohm-cm): 29.18

Average 45° Bond Strength (lbs)

A. Room Temperature: 0.67

B. Elevated Temperature (200°C) 0.49

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. The wetting interface chemical reaction on a copper surface is the formation of a ternary or a combination of binary solid solutions of copper, lead and indium. Since the indium content of this solder alloy is relatively low, no copper-indium intermetallic compounds are formed at the copper interface.

2. During the solder coating operation of the copper clad board material, it was discovered that the interface wetting reaction produced only marginal results.

Solder Alloy: 80Pb20In

Liquidus Temperature:	280°C
Solidus Temperature:	260°C

Solderability Rating

A. Copper Surface:	Average
B. Au-Plated Kovar Surface:	Average
C. Kovar Surface:	Poor

Electrical Resistivity ($x10^{-6}$ ohm-cm): 36.09

Average 45° Bond Strength (lbs)

A. Room Temperature:	1.17
B. Elevated Temperature (200°C)	0.27

Metallurgical Compatibility

A. Copper Base Material:	Good
B. Au-Plated Kovar Base Material:	Unacceptable

Comments and Conclusions

1. Interface cracking occurs on the gold-plated Kovar surface during high temperature exposure. This alloy is therefore considered to be unacceptable for high temperature application.

2. For this higher indium content solder alloy, the wetting reaction on a copper surface is the formation of the Cu_9In_7 intermetallic compound. Therefore, the copper wetting reaction changes from a solid solution reaction to an intermetallic compound reaction somewhere between six and twenty percent indium content.

Solder Alloy: 60Pb40In

Liquidus Temperature:	233°C
Solidus Temperature:	213°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): 33.40

Average 45^{O} Bond Strength (lbs)

A. Room Temperature: 0.85

B. Elevated Temperature (200^{O}C) 0.02

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Unacceptable

Comments and Conclusions

1. Interface cracking occurs on the gold-plated Kovar surface prior to and during high temperature exposure. This alloy is therefore considered to be unacceptable.

2. This solder alloy produces joints of zero elevated temperature bond strength properties and is therefore considered to be unacceptable for high temperature type applications.

Solder Alloy: 98Pb2Sb

Liquidus Temperature: 315^{O}C

Solidus Temperature: 302^{O}C

Solderability Rating

A. Copper Surface: No Wetting

B. Au-Plated Kovar Surface: Average

C. Kovar Surface: Fair

Electrical Resistivity ($x10^{-6}$ ohm-cm): NTP

Average 45^{O} Bond Strength (lbs)

A. Room Temperature: NTP

B. Elevated Temperature (200^{O}C): NTP

Metallurgical Compatibility

A. Copper Base Material: NTP

B. Au-Plated Kovar Base Material: NTP

Comments and Conclusions

Due to the inability to adequately wet a copper surface, this solder alloy was screened from the original candidate alloy list following evaluation of the solderability results.

Solder Alloy: 89Pb11Sb

Liquidus Temperature: 252°C

Solidus Temperature: 252°C

Solderability Rating

A. Copper Surface: Poor

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): NTP

Average 45° Bond Strength (lbs)

A. Room Temperature: NTP

B. Elevated Temperature (200°C): NTP

Metallurgical Compatibility

A. Copper Base Material: NTP

B. Au-Plated Kovar Base Material: NTP

Comments and Conclusions

Due to the inability to adequately wet a copper surface, this alloy was screened from the original candidate alloy list following evaluation of the solderability results.

Solder Alloy: 82Pb18Sb

Liquidus Temperature: 315°C

Solidus Temperature: 257°C

Solderability Rating

A. Copper Surface: Poor

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): NTP

Average 45^{o} Bond Strength (lbs)

A. Room Temperature: NTP

B. Elevated Temperature ($200^{o}C$): NTP

Metallurgical Compatibility

A. Copper Base Material: NTP

B. Au-Plated Kovar Base Material: NTP

Comments and Conclusions

Due to the inability to adequately wet a copper surface, this solder alloy was screened from the original candidate alloy list following evaluation of the solderability results.

Solder Alloy: 96Pb4Sn

Liquidus Temperature: $321^{o}C$

Solidus Temperature: $310^{o}C$

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Average

Electrical Resistivity ($x10^{-6}$ ohm-cm): 22.59

Average 45^{o} Bond Strength (lbs)

A. Room Temperature: 1.42

B. Elevated Temperature ($200^{o}C$): 0.65

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. Since the tin content of this alloy is relatively low, the copper-tin intermetallic compound formation rate is slow.

2. This solder alloy produces joints of exceptional strength properties but only marginal solderability characteristics.

Solder Alloy: 90Pb10Sn

Liquidus Temperature: $305^{\circ}C$

Solidus Temperature: $278^{\circ}C$

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Poor

Electrical Resistivity ($x10^{-6}$ ohm-cm): 20.30

Average 45° Bond Strength (lbs)

A. Room Temperature: 1.18

B. Elevated Temperature ($200^{\circ}C$): 0.60

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. As is expected from a lead rich solder alloy, the room temperature and elevated temperature bond strength properties are excellent.

2. The electrical resistivity properties and solderability characteristics are considered to be marginal.

Solder Alloy: 84Pb16Sn

Liquidus Temperature: $292^{o}C$

Solidus Temperature: $191^{o}C$

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Average

C. Kovar Surface: Good

Electrical Resistivity ($x10^{-6}$ ohm-cm): 19.49

Average 45^{o} Bond Strength (lbs)

A. Room Temperature: 1.27

B. Elevated Temperature ($200^{o}C$): 0.28

Metallurgical Compatibility

A. Copper Base Material: Unacceptable

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. Since the reported solidus temperature is below $200^{o}C$, the copper-tin intermetallic compound formation rate for this solder alloy was accelerated by a liquid-solid reaction during high temperature exposure. As a result, an excessive amount of copper-tin intermetallic compound formed on the copper surface.

2. The reported elevated temperature properties are considered to be unacceptable for high temperature applications.

Solder Alloy: 97Cd3Sb

Liquidus Temperature: $316^{o}C$

Solidus Temperature: $296^{o}C$

Solderability Rating

A. Copper Surface: Excellent

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Fair

Electrical Resistivity (x10^{-6} ohm-cm): 9.03

Average 45° Bond Strength (lbs)

A. Room Temperature: 1.01

B. Elevated Temperature (200°C): 0.61

Metallurgical Compatibility

A. Copper Base Material: Unacceptable

B. Au-Plated Kovar Base Material: Poor

Comments and Conclusions

1. Since the copper interface wetting reaction produces cracks, this alloy is considered to be unacceptable.

2. The SEM results indicate the antimony constituent did not enter into the copper interface reaction. Therefore, it is concluded that the antimony merely catalyzed the cadmium-copper intermetallic compound reaction.

Solder Alloy: 91Cd9Sb

Liquidus Temperature: 294°C

Solidus Temperature: 294°C

Solderability Rating

A. Copper Surface: Excellent

B. Au-Plated Kovar Surface: Average

C. Kovar Surface: Average

Electrical Resistivity (x10^{-6} ohm-cm): 10.99

Average 45° Bond Strength (lbs)

A. Room Temperature: 0.92

B. Elevated Temperature (200°C): 0.39

Metallurgical Compatibility

A. Copper Base Material: Unacceptable

B. Au-Plated Kovar Base Material: Poor

Comments and Conclusions

1. Since the copper interface wetting reaction produces cracks, this alloy is considered to be unacceptable.

2. As with the previous solder alloy, the antimony constituent does not directly enter into the cadmium-copper intermetallic compound reaction. It merely acts as a catalyst thereby accelerating the reaction.

3. Due to the brittle as-cast nature of this solder alloy, it was necessary to hot roll the preform sheet material.

Solder Alloy: 88Cd12Sb

Liquidus Temperature:	299°C
Solidus Temperature:	294°C

Solderability Rating

A. Copper Surface:	Excellent
B. Au-Plated Kovar Surface:	Average
C. Kovar Surface:	Poor
Electrical Resistivity ($x10^{-6}$ ohm-cm):	12.72

Average 45° Bond Strength (lbs)

A. Room Temperature:	0.77
B. Elevated Temperature (200°C):	0.91

Metallurgical Compatibility

A. Copper Base Material:	Unacceptable
B. Au-Plated Kovar Base Material:	Poor

Comments and Conclusions

1. Since the copper interface wetting reaction produces cracks, this alloy is considered to be unacceptable.

2. Since the mode of failure of the elevated temperature bond strength test is through the copper clad material, it is concluded the antimony constituent embrittles the copper base metal through a pseudo age hardening type mechanism suffered during high temperature exposure.

3. Due to the brittle as-cast nature of this alloy, it was necessary to hot roll the preform sheet material.

Solder Alloy: 62Cd38Zn

Liquidus Temperature:	313°C
Solidus Temperature:	269°C

Solderability Rating

A. Copper Surface:	Average
B. Au-Plated Kovar Surface:	Average
C. Kovar Surface:	Good

Electrical Resistivity ($x10^{-6}$ ohm-cm): 7.31

Average 45° Bond Strength (lbs)

A. Room Temperature:	1.05
B. Elevated Temperature (200°C):	0.00

Metallurgical Compatibility

A. Copper Base Material:	Unacceptable
B. Au-Plated Kovar Base Material:	Fair

Comments and Conclusions

1. The high magnification optical examination revealed that solder alloy degradation occurs during high temperature exposure.

2. Inferior elevated temperature properties renders this alloy unsuitable for high temperature type applications.

3. Preliminary tests indicate that the $AuZn_8$ phase which formed on the gold-plated Kovar surface is ductile and is therefore a desirable interface product.

4. Figure 34 (view a) illustrates the chemical gradient from the copper base material across the soldered interface into the solder alloy. Due to the relatively high zinc content, this alloy produces an excessive amount of $Cu_3Cd_3Zn_4$ ternary intermetallic compound. The solder alloy (view b) immediately adjacent to the ternary intermetallic compound layer has suffered some plastic deformation due to a volume expansion difference between the solder alloy and the $Cu_3Cd_3Zn_4$ phase. The rapid and excessive ternary intermetallic compound formation rate is believed to be responsible for the low elevated temperature properties.

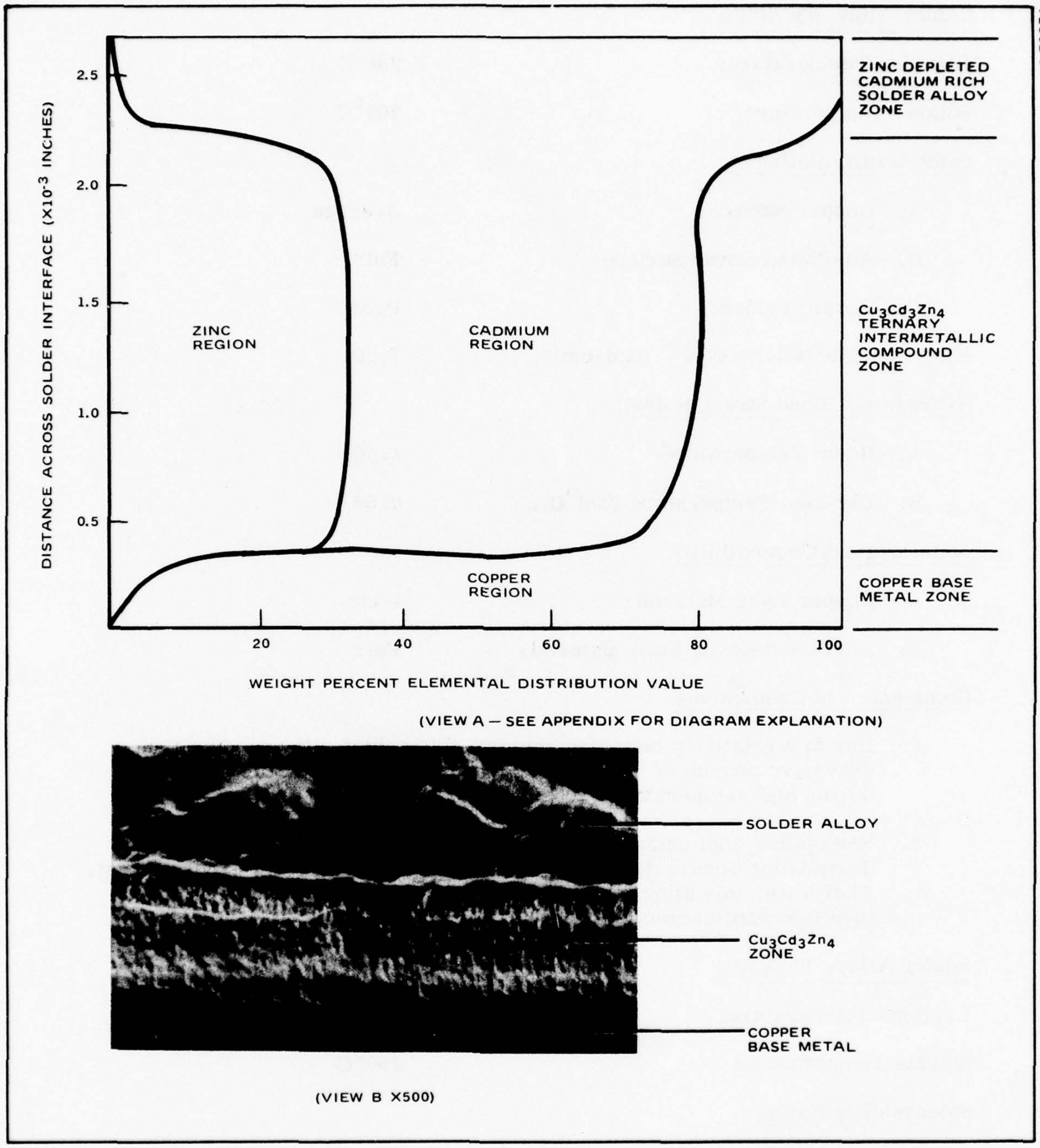


Figure 34. Copper Surface 62 Cd 38 Zn Solder Alloy Interface Reaction (Following Exposure to 200°C for 200 Hours)

Solder Alloy: 83Cd17Zn

Liquidus Temperature:	268°C
Solidus Temperature:	268°C

Solderability Rating

A. Copper Surface:	Average
B. Au-Plated Kovar Surface:	Fair
C. Kovar Surface:	Poor
Electrical Resistivity ($x10^{-6}$ ohm-cm):	7.60

Average 45° Bond Strength (lbs)

A. Room Temperature:	1.46
B. Elevated Temperature (200°C):	0.53

Metallurgical Compatibility

A. Copper Base Material:	Poor
B. Au-Plated Kovar Base Material:	Fair

Comments and Conclusions

1. Due to a relatively high zinc content, this solder alloy produces an excessive amount of the $Cu_3Cd_3Zn_4$ ternary intermetallic compound during high temperature exposure.

2. The optical high magnification examination revealed that solder alloy degradation occurs during the extended high temperature exposure test. Therefore, this alloy is not considered to be suited for high temperature type applications.

Solder Alloy: 98Cd2Zn

Liquidus Temperature:	318°C
Solidus Temperature:	290°C

Solderability Rating

A. Copper Surface:	Excellent
B. Au-Plated Kovar Surface:	Fair
C. Kovar Surface:	Fair

Electrical Resistivity ($x10^{-6}$ ohm-cm): 7.53

Average 45^{o} Bond Strength (lbs)

A. Room Temperature: 2.10

B. Elevated Temperature ($200^{o}C$): 0.21

Metallurgical Compatibility

A. Copper Base Material: Excellent

B. Au-Plated Kovar Base Material: Fair

Comments and Conclusions

1. Figure 35 (view a) reveals the $Cu_3Cd_3Zn_4$ (approximate composition) intermetallic compound copper interface reaction to terminate when the solder alloy immediately adjacent to the copper surface is thoroughly depleted of the zinc constituent. Once the ternary reaction is complete, the resulting $Cu_3Cd_3Zn_4$ intermetallic layer serves as a barrier thereby precluding the formation of any binary cadmium-copper intermetallics such as the $CuCd_3$ phase shown in Figure 33. The relatively low zinc content accounts for the resulting thin ternary intermetallic compound layer (view b).

2. Due to solder alloy degradation at elevated temperatures and inferior high temperature properties, this particular alloy is considered to be unacceptable.

Solder Alloy: 97.5Pb2.5Ag

Liquidus Temperature: $310^{o}C$

Solidus Temperature: $310^{o}C$

Solderability Rating

A. Copper Surface: Fair

B. Au-Plated Kovar Surface: Excellent

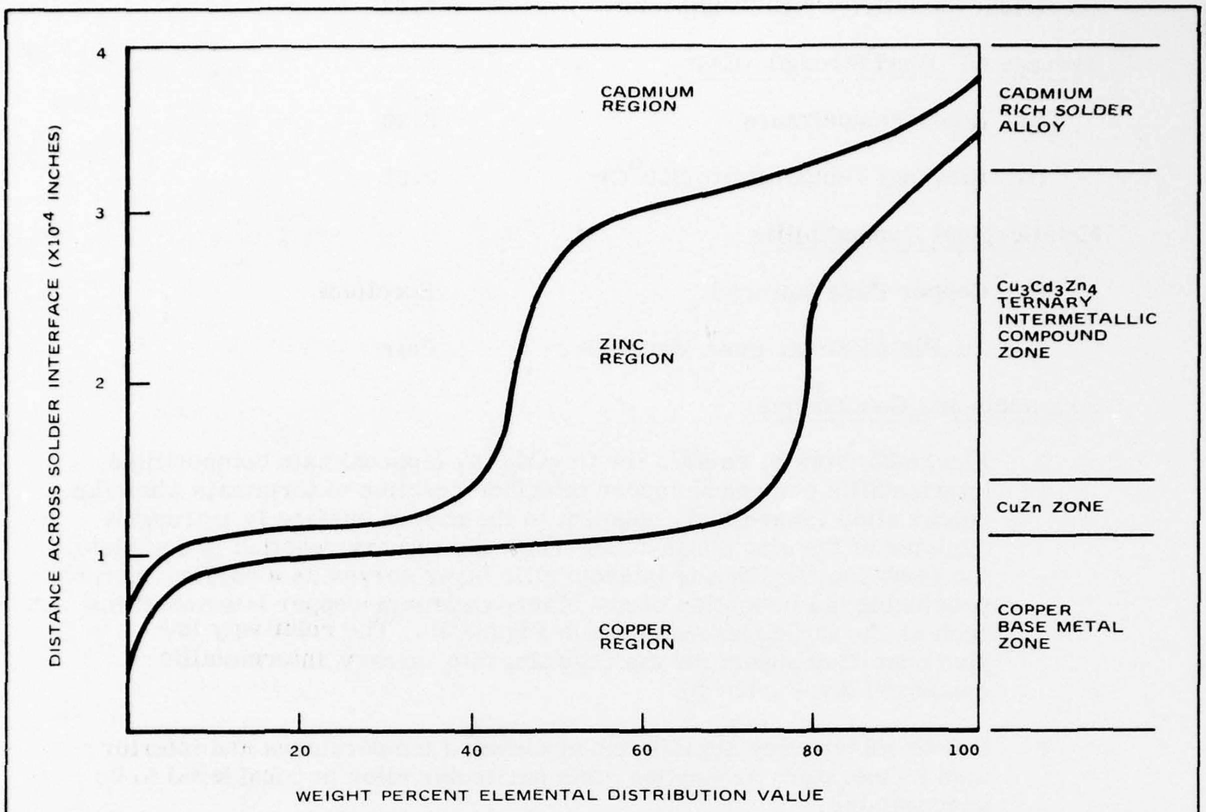
C. Kovar Surface: No Wetting

Electrical Resistivity ($x10^{-6}$ ohm-cm): NTP

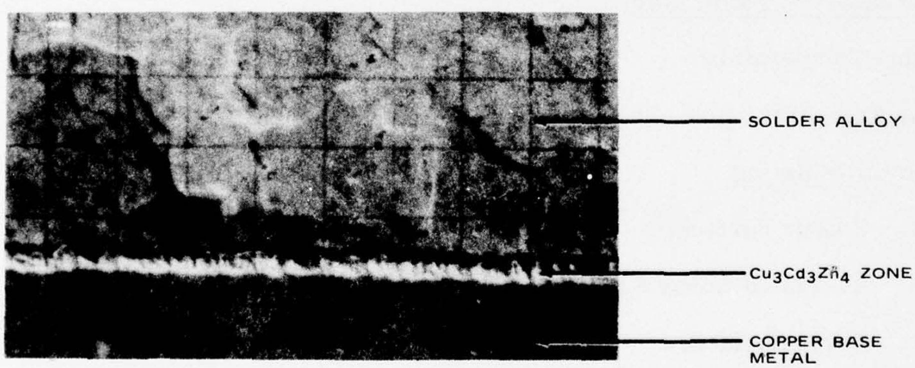
Average 45^{o} Bond Strength

A. Room Temperature: NTP

B. Elevated Temperature ($200^{o}C$): NTP



(VIEW A — SEE APPENDIX FOR DIAGRAM EXPLANATION)



(VIEW B X500)

Figure 35. Copper Surface 98 Cd 2 Zn Solder Alloy Interface Reaction (Following Exposure to 200°C for 200 Hours)

Metallurgical Compatibility

A. Copper Base Material: NTP

B. Au-Plated Kovar Base Material: NTP

Comments and Conclusions

Due to the inability to adequately wet a Kovar surface, this alloy was screened from the original candidate alloy list following evaluation of the solderability results.

ALLOY SCREENING PROCEDURE AND RESULTS

In an effort to screen the remaining twenty candidate alloys, each property (mechanical strength, solderability, metallurgical compatibility, electrical resistivity, toxicity and cost) was compared to the corresponding property of the other solder alloys and assigned a relative rating value. The highest values were assigned to properties with the most desirable characteristics. Each general property category was assigned a specific maximum weight value which is directly proportional to the relative importance of the particular property in question. Therefore, the assigned rating value for each alloy property is equal to a number between zero and the maximum weight value. Table 11 lists the assigned rating values and maximum weights for each property and solder alloy combination.

Solder joints that showed evidence of interface cracking were automatically assigned a zero metallurgical compatibility rating value for the applicable base material and solder alloy combination. Solder alloys that exhibited a zero mechanical strength rating, poor solderability characteristics and/or a zero metallurgical compatibility rating value resulted in a low total value because these properties were weighted heavily. Consequently, the solder alloys that possess poor major property characteristics were ultimately screened from the Task II candidate alloy list.

As shown by Table 11, high lead-low tin and high lead-low cadmium content solder alloys produce the highest alloy characterization total. Therefore, these two type optimum compositions were selected for further modifications and testing during the Task II phase of the program.

TABLE 11. ALLOY CHARACTERIZATION SCREENING RESULTS

Solder Alloy	Solderability			Mechanical Strength		Metallurgical Compatibility		Electrical Resistivity	Cost	Toxicity	Total
	Copper Surface	Kovar Surface	Au-Kovar Surface	Room Temperature	200°C	Copper Surface	Au-Kovar Surface				
100Sn	8	4	5	6	3	7	1	4	2	5	45
99Sn1Sb	4	4	3	6	1	7	1	4	2	5	37
90Sn10Sb	4	4	4	2	2	7	1	3	2	5	34
82Sn18Sb	4	3	4	3	3	7	1	3	2	5	35
*97Pb3Cd	6	1	3	7	9	8	4	3	5	4	50
*83Pb17Cd	6	3	3	6	10	5	3	3	4	3	46
50Pb50Cd	8	3	3	5	3	5	0	4	3	2	36
92Cd8Pb	8	3	5	6	3	3	4	5	2	0	39
94Pb6In	6	4	4	5	4	9	1	1	1	5	40
80Pb20In	6	1	3	7	2	8	0	0	0	5	32
60Pb40In	6	3	4	6	0	7	0	0	0	5	31
*96Pb4Sn	6	3	4	9	6	6	3	2	5	5	49
*90Pb10Sn	6	1	4	7	6	8	4	3	4	5	48
84Pb16Sn	6	4	3	8	2	1	3	3	4	5	39
97Cd3Sb	10	2	4	7	6	0	5	5	2	0	41
91Cd9Sb	10	3	3	6	3	0	5	4	2	0	36
88Cd12Sb	10	1	3	5	9	0	5	4	2	1	40
98Cd2Zn	10	2	2	10	2	8	5	5	2	0	46
83Cd17Zn	6	1	2	10	5	1	3	5	2	1	36
62Cd38Zn	6	4	2	7	0	0	3	5	3	2	32
Maximum Weight Value	10	5	5	10	10	10	5	5	5	5	70

*Selected for modification in Task II

CONCLUSION

Figure 35 illustrates the ability of a particular solder alloy (98Cd2Zn) to control and contain an intermetallic compound copper interface reaction. This is accomplished by forming a high zinc content ternary intermetallic compound during high temperature exposure which subsequently acts as a barrier precluding further intermetallic formation. The amount of ternary intermetallic compound produced during high temperature exposure is a function of the zinc content of the solder alloy. For example, 38% zinc in cadmium forms 0.00160 inches of $Cu_3Cd_3Zn_4$ (Figure 34) where 2% zinc in cadmium produces on 0.00022 inches. Therefore, it is considered beneficial for a solder alloy that is used for high temperature applications on copper surfaces to contain small amounts of zinc with cadmium. This combination appears to limit intermetallic compound formation on copper base materials.

In an effort to combine the apparent advantages of this intermetallic barrier principle with the advantages of the excellent elevated temperature properties of lead base solder alloys, lead-cadmium-zinc and lead-tin-zinc ternary solder systems were selected for test and evaluation during the Task II phase of the program. The effect of small amounts (0.5 - 2.0 weight %) of copper in lead-tin and lead-cadmium systems are also of interest because it is felt small additions of copper in the solder alloy may retard the copper-tin and copper-cadmium intermetallic reactions.

Comments and Conclusions

A. Due to twice the zinc content, this alloy produces twice as much $Cu_3Cd_3Zn_4$ intermetallic compound at a copper interface than does the 90Pb 9Cd 1Zn solder alloy. It is therefore concluded that the optimum zinc content for lead-cadmium-zinc solder alloys is within the 0.5 to 1.0 percent range. If the zinc composition is maintained in this range the $Cu_3Cd_3Zn_4$ intermetallic barrier is formed without producing excessive and detrimental phases at the solder interface.

B. A more significant drop in strength at high temperature occurred with this alloy than with the 90 Pb 9Cd 1 Zn solder alloy.

CONCLUSIONS

The test data reveals that the 90Pb 9Cd 1 Zn alloy forms the least amount of intermetallic compound during high temperature exposure. It was discovered during the Task I and Task II efforts that small amounts of zinc in the presence of cadmium will form the $Cu_3Cd_3Zn_4$ (approximate atomic composition) ternary intermetallic compound on a copper surface during extended exposure to elevated temperatures. The thickness of this intermetallic layer is entirely dependent on the zinc content of the solder alloy. The higher the zinc concentration the more severe the resulting ternary intermetallic compound formation. This solder alloy forms only 1×10^{-4} inches of intermetallic (Table 16) before the solder immediately adjacent to the copper interface is depleted of zinc content. Once all the accessible zinc is consumed, the ternary reaction subsides. The resulting $Cu_3Cd_3Zn_4$ layer then acts as a barrier thereby precluding subsequent formation of binary cadmium-copper intermetallic compounds. The solder interface is then considered to be inert regardless of continued long term exposure to elevated temperatures. The lead constituent provides excellent elevated temperature properties while the cadmium and zinc constituents increase solderability and minimize the formation of intermetallic compounds.

SECTION 3
TASK II ALLOY MODIFICATION AND OPTIMIZATION

Since the 90Pb 9Cd 1Zn alloy of Task II proved to be superior it was selected for final evaluation in Task III. It is of interest to compare it to a high temperature lead - tin alloy which also had a high rating in Task I, viz. 90 Pb 10Sn. For these reasons these two alloys were chosen for Task III, the final characterization study.

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TASK II ALLOY MODIFICATION AND OPTIMIZATION

INTRODUCTION

The high lead-low tin and high lead-low cadmium binary systems were selected for further modification. In an effort to combine the apparent advantages of the intermetallic barrier principle with the advantages of the excellent elevated temperature properties of lead base solder alloys, lead-cadmium-zinc and lead-tin-zinc ternary solder systems were selected for test and evaluation during the Task II phase of the program. The effect of small amounts (0.5 - 2.0 weight %) of copper in lead-tin and lead-cadmium systems are also of interest because it is felt small additions of copper in the solder alloy may retard the copper-tin and copper-cadmium intermetallic reactions.

In order to maintain test result consistency throughout the Task I and Task II efforts of the program, the exact same tests and testing procedures were utilized for the Task II candidate solder alloys as were used for the Task I candidate solder alloys. Alloy preparation procedures, preform fabrication and alloy characterization tests remained unchanged so that the resulting Task II alloy properties could be directly compared with the properties of the candidate alloys of Task I. In this manner, an objective method for the determination of improvement of critical properties could be realized.

TASK II CANDIDATE ALLOY LIST

The following ternary alloys have been selected for further evaluation.

a. 89.5Pb 10Sn 0.5Cu
b. 90Pb 8Sn 2Cu
c. 90Pb 9Sn 1Zn
d. 93Pb 5Sn 2Zn
e. 89.5Pb 10Cd 0.5Cu
f. 90Pb 8Cd 2Cu
g. 90Pb 9Cd 1Zn
h. 93Pb 5Cd 2Zn

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CHEMICAL ANALYSIS RESULTS

A sample from each solder alloy melt was subjected to wet and spectrographic quantitative chemical analysis to determine the actual chemistry of each Task II alloy in regard to constituent and impurity content. The results are listed in Table 12.

TABLE 12. TERNARY SOLDER ALLOY QUANTITATIVE CHEMICAL TEST RESULTS

	Metallic Element – Wt. %					
Solder Alloy	Cd	Cu	Pb	Zn	Sn	Impurities (Total)
89.5Pb 10Sn 0.5Cu	--	0.47	Rem	--	10.0	<0.1%
90Pb 8Sn 2Cu	--	1.99	Rem	--	7.8	<0.1%
90Pb 9Sn 1Zn	--	--	Rem	0.98	9.3	<0.1%
93Pb 5Sn 2Zn	--	--	Rem	2.2	5.2	<0.1%
89.5Pb 10Cd 0.5Cu	9.6	0.48	Rem	--	--	<0.1%
90Pb 8Cd 2Cu	7.0	2.0	Rem	--	--	<0.1%
90Pb 9Cd 1Zn	8.7	--	Rem	0.84	--	<0.1%
93Pb 5Cd 2Zn	4.8	--	Rem	1.8	--	<0.1%

COOLING CURVE DETERMINATION

The solidus and liquidus temperatures of these ternary alloys cannot be accurately predicted from binary phase diagrams. Modification of a binary system by the addition of a ternary element may alter melting point values and phase distribution characteristics of the original alloy. Solidus and liquidus temperature values for each of the Task II ternary solder alloys were determined experimentally from cooling curve data and are listed in Table 13.

SOLDERABILITY TEST RESULTS

The solderability test apparatus and procedures used for the Task II alloys were exactly the same as the apparatus and procedures that were used for the solder alloys of Task I. The solderability test specimens for each Task II alloy are shown in Figures 36 through 43. The solderability spread rating values are listed in Table 14. Due to the relatively high copper content, the 90 Pb 8Cd 2Cu alloy proved to be too viscous and was eliminated from the Task II candidate alloy list.

Generally, the solderability spread results for the Pb-Sn-Cu alloys show good wetting on all three base materials. The addition of zinc adversely affects wetting on copper and Kovar when tin is present in the solder alloy. The Pb-Cd-Zn alloys proved to wet gold plated Kovar and copper surfaces quite well.

TABLE 13. TERNARY SOLDER ALLOY SOLIDUS AND LIQUIDUS TEMPERATURE DETERMINATION RESULTS

Solder Alloy	Liquidus Temp. ^oC	Solidus Temp. ^oC
89.5Pb10Sn.5Cu	299	284
90Pb8Sn2Cu	307	302
90Pb9Sn1Zn	290	282
93Pb5Sn2Zn	301	295
89.5Pb10Cd.5Cu	277	250
90Pb8Cd2Cu	294	247
90Pb9Cd1Zn	260	238
93Pb5Cd2Zn	287	245

Solderability Test Specimens.

72602-36

Figure 36. X1.25 – 89.5 Pb 10 Sn 0.5 Cu

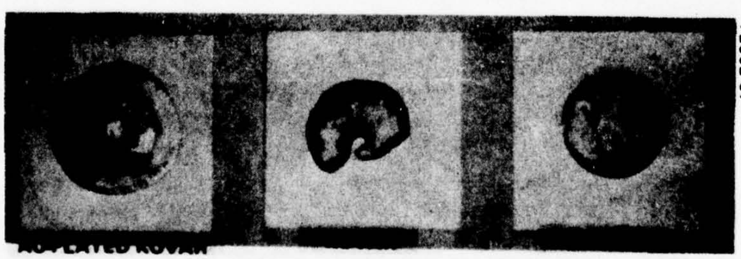

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Figure 37. X1.25 – 90 Pb 8 Sn 2 Cu

Solderability Test Specimens.

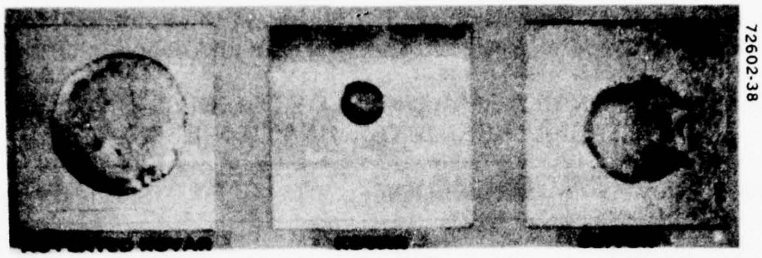


Figure 38. X1.25 – 90 Pb 9 Sn 1 Zn

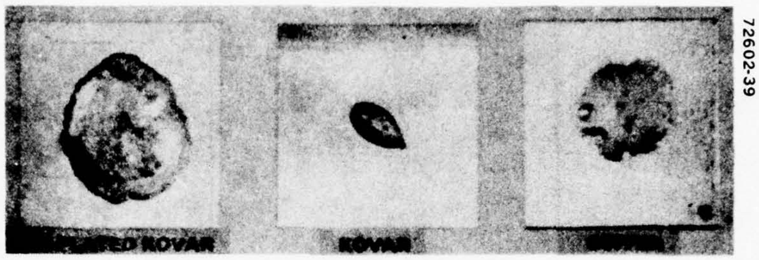


Figure 39. X1.25 – 93 Pb 5 Sn 2 Zn

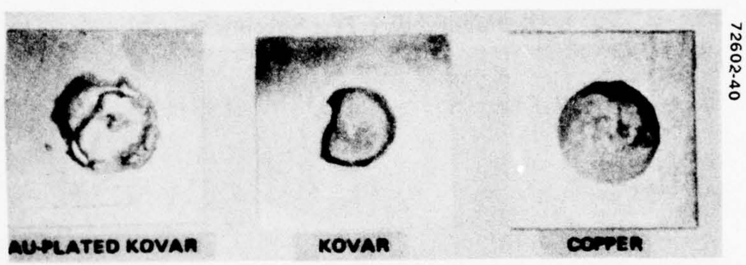


Figure 40. X1.25 – 89.5 Pb 10 Cd 0.5 Cu

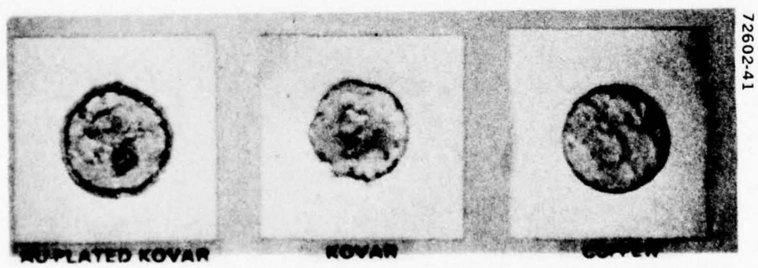
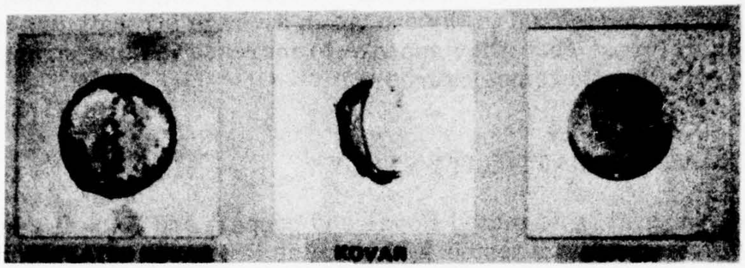


Figure 41. X1.25 – 90 Pb 8 Cd 2 Cu

Solderability Test Specimens.

72602-42

Figure 42. X1.25 – 90 Pb 9 Cd 1 Zn



72602-43

Figure 43. X1.25 – 93 Pb 5 Cd 2 Zn

TABLE 14. OVERALL TERNARY CANDIDATE ALLOY SOLDERABILITY SPREAD RATING RESULTS

Solder Alloy	Base Material			Total Rating
	Au-Plated Kovar	Kovar	Copper	
89.5Pb 10Sn 0.5Cu	4	4	3	11
90Pb 8Sn 2Cu	4	3	3	10
90Pb 9Sn 1Zn	5	0	2	7
93Pb 5Sn 2Zn	4	0	2	6
89.5Pb 10Cd 0.5Cu	1	3	3	7
90Pb 8Cd 2Cu	1*	1*	1*	3
90Pb 9Cd 1Zn	4	2	3	9
93Pb 5Cd 2Zn	4	1	3	8

*Due to conglomeration of the high temperature $CuCd_3$ phase, this alloy did not flow properly (see Figure 41).

45° BOND STRENGTH TEST RESULTS

The 45° mechanical bond strength testing equipment and procedures utilized for the Task II candidate alloys were identical to the previously reported test set-ups and procedures used for the binary solder alloys of Task I. In addition to the room temperature and elevated temperature bond tests for samples tested in the "as soldered" condition, room temperature and elevated temperature tests were also performed on samples that were exposed to 200°C for 200 hours. The average bond strength results for each condition and testing temperature combination are listed in Table 15. Ten individual pull tests were performed for each combination.

The test data reveals that the 200°C exposure for 200 hours had no significant affect on the respective room temperature and elevated temperature bond strength properties. The 90Pb 9Cd 1Zn alloy seems to have the most stable strength properties as related to the change in average strength due to a change in testing temperature. This alloy appears to increase in bond strength with extended aging at elevated temperatures.

METALLURGICAL COMPATIBILITY STUDY

Each base material (gold plated Kovar and copper) and Task II candidate solder alloy combination was tested to determine the intermetallic compound growth rate experienced during soldering and high temperature exposure (200°C for 200 hours). SEM line scan and x-ray quantitative chemical analyses results are listed in Tables 16 and 17.

ELECTRICAL RESISTIVITY RESULTS

The electrical resistivity of each Task II alloy was measured using the same sample configuration and testing methods that were used for the solder alloys of Task I. The test results shown in Table 18 reveal that the electrical resistivity decreases as the combined cadmium, zinc, tin and/or copper increases.

ALLOY CHARACTERIZATION SCREENING RESULTS

The same screening procedure used for the Task I alloys was also used for the candidate alloys of Task II. Table 19 illustrates the relative rating values assigned to the property characteristics for each Task II solder alloy. The 90Pb 9Cd 1Zn solder alloy shows the highest total value and was therefore selected for study during the Task III effort of the program.

TABLE 15. TERNARY ALLOY AVERAGE BOND STRENGTH RESULTS

Solder Alloy	As Soldered Condition**				200C for 200 Hours Condition**			
	Testing Temp		$20^{o}C$* Failure Mode	$200^{o}C$* Failure Mode	Testing Temp		$20^{o}C$* Failure Mode	$200^{o}C$* Failure Mode
	$20^{o}C$	$200^{o}C$			$20^{o}C$	$200^{o}C$		
89.5Pb 10Sn .5Cu	0.86	0.42	LS	LS	0.88	0.47	LS&S	LS&S
90Pb 8Sn 2Cu	0.95	0.45	LS&S	LS	0.95	0.41	LS&S	LS&S
90Pb 9Sn 1Zn	1.05	0.67	LS	LS	1.12	0.55	LS	LS
93Pb 5Sn 2Zn	1.20	0.75	LS	LS	1.53	0.75	LS&S	LS&S
89.5Pb 10Cd .5Cu	1.24	0.52	LS	LS	1.60	0.81	LS	LS
90Pb 9Cd 1Zn	0.64	0.59	LS	LS&S	1.13	0.78	S	S
93Pb 5Cd 2Zn	0.95	0.61	LS&S	LS&S	1.32	0.66	S	S

* LS – Lead to solder failure
S – Solder failure
**The strength values reported are based upon a 0.017 inch lead width.

TABLE 16. TERNARY METALLURGICAL COMPATIBILITY RESULTS (COPPER BASE MATERIAL)

Solder Alloy	As Soldered Condition	Phase Thickness $X10^{-4}$ in.	200°C for 200 Hours Condition	Phase Thickness $X10^{-4}$ in.	Net Change In Thickness $X10^{-4}$ in.	Remarks
89.5Pb 10Sn 0.5Cu	Cu_3Sn	1.20	Cu_3Sn Cu_6Sn_5	2.50 0.62	1.92	The 0.5% copper content in this solder alloy did seem to reduce the intermetallic compound growth rate when compared with the Pb-Sn alloys of Task I.
90Pb 8Sn 2Cu	None	--	Cu_3Sn	1.88	1.88	The 2% copper addition had little more effect on intermetallic compound growth rate reduction than did the 0.5% addition for the 89.5Pb 10Sn 0.5Cu alloy.
93Pb 5Sn 2Zn	Zn (CuZn)	1.56	CuZn	3.22	1.66	1- The as soldered zinc rich interface is also copper rich (possibly CuZn and Zn). 2- Due to the interface reaction, the solder alloy adjacent to the CuZn layer is depleted of zinc content.
90Pb 9Sn 1Zn	Zn (CuZn)	1.40	CuZn	2.81	1.41	1- The as soldered zinc rich interface is also copper rich (possibly CuZn and solder) 2- The solder alloy adjacent to the interface is void of zinc content.

TABLE 16. TERNARY METALLURGICAL COMPATIBILITY RESULTS (COPPER BASE MATERIAL) (Continued)

Solder Alloy	As Soldered Condition	Phase Thickness $X10^{-4}$ in.	$200^{o}C$ for 200 Hours Condition	Phase Thickness $X10^{-4}$ in.	Net Change In Thickness $X10^{-4}$ in.	Remarks
89.5Pb 10Cd 0.5Cu	None	--	Cu_5Cd_8	2.08	2.08	The 0.5% copper content of this alloy seemed to reduce the intermetallic compound growth rate when compared to the Pb-Cd alloys of Task I.
90Pb 9Cd 1Zn	Zn (CuZn)	0.90	CuZn $Cu_3Cd_3Zn_4$	1.0 1.0	1.10	1- The as soldered zinc rich interface is also copper rich. 2- The solder alloy adjacent to the $Cu_3Cd_3Zn_4$ layer is depleted of zinc content.
93Pb 5Cd 2Zn	CuZn	1.25	CuZn $Cu_3Cd_3Zn_4$	2.50 1.00	2.25	1- The solder alloy adjacent to the $Cu_3Cd_3Zn_4$ layer is void of zinc content. 2- Twice as much intermetallic compound was formed in this alloy as was for the 90Pb 9Cd 1Zn alloy.

TABLE 17. TERNARY METALLURGICAL COMPATIBILITY RESULTS (GOLD PLATED KOVAR BASE MATERIAL)

Solder Alloy	As Soldered Condition	Phase Thickness $X10^{-4}$ in.	$200^{o}C$ for 200 Hours Condition	Phase Thickness $X10^{-4}$ in.	Net Change In Thickness $X10^{-4}$ in.	Remarks
89.5Pb 10Sn 0.5Cu	None	--	None	--	--	1- The tin-gold inter-metallic compound was in particle form prior to exposure. 2- The tin-gold particles were dissolved in the solder matrix during exposure.
90Pb 8Sn 2Cu	None	--	None	--	--	1- The tin-gold inter-metallic compound was in particle form prior to exposure. 2- The tin-gold particles were dissolved in the solder matrix during exposure.
93Pb 5Sn 2Zn	None	--	None	--	--	The gold-zinc intermetallic compound was dissolved by the tin in the solder alloy during the soldering operation.
90Pb 9Sn 1Zn	None	--	None	--	--	The gold-zinc intermetallic compound was dissolved by the tin in the solder alloy during the soldering operation.

TABLE 17. TERNARY METALLURGICAL COMPATIBILITY RESULTS (GOLD PLATED KOVAR BASE MATERIAL) (Continued)

Solder Alloy	As Soldered Condition	Phase Thickness X10^{-4} in.	200°C for 200 Hours Condition	Phase Thickness X10^{-4} in.	Net Change In Thickness X10^{-4} in.	Remarks
89.5Pb 10Cd 0.5Cu	See Remark No. 1	--	See Remark No. 1	--	--	1- The cadmium-gold intermetallic compound ($AuCd_3$) was in layer and particle form. 2- No change in structure was noted following exposure (the $AuCd_3$ layer was partially dissolved by the solder).
90Pb 9Cd 1Zn	$AuZn_3$ $AuZn_3$ +Cd	1.56 1.88	$AuZn_3$ $AuZn_3$ +Cd	1.56 1.91	0 0.03	1- The $AuZn_3$ intermetallic compound layer formed during soldering shows evidence of a secondary dissolution reaction by cadmium. 2- No change in structure was noted following exposure.
93Pb 5Cd 2Zn	None	--	None	--	--	The gold-zinc intermetallic compound was in particle form prior to and following exposure.

TABLE 18. TERNARY ALLOY ELECTRICAL RESISTIVITY DETERMINATION RESULTS

Solder Alloy	Electrical Resistivity ($\times 10^{-6}$ ohm-cm)
89.5Pb 10Sn 0.5Cu	23.07
90Pb 8Sn 2Cu	21.79
93Pb 5Sn 2Zn	20.39
90Pb 9Sn 1Zn	20.94
89.5Pb 10Cd 0.5Cu	15.82
90Pb 9Cd 1Zn	17.69
90Pb 5Cd 2Zn	18.87

CANDIDATE ALLOY SUMMARY

Solder Alloy 89.5 Pb 10Sn 0.5Cu

Liquidus Temperature: 299°C
Solidus Temperature: 284°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Good

Electrical Resistivity: 23.07×10^{-6} ohm-cm

Average 45° Bond Strength (lbs.)

A. As Soldered Condition
Tested at Room Temperature: 0.86

B. As Soldered Condition
Tested at 200°C: 0.42

C. 200°C for 200 Hours Condition
Tested at Room Temperature 0.88

D. 200°C for 200 hours Condition
Tested at 200°C: 0.47

Metallurgical Compatibility Rating

A. Copper Base Material: Average

B. Au-Plated Kovar Material: Average

Comments and Conclusions

A. Since the respective bond strength results remained unchanged, it was concluded that the high temperature exposure (200°C for 200 hours) had little effect in changing the as soldered bond strength properties.

B. Since the high temperature bond strength properties are only 50 percent of the room temperature properties, the alloy is considered to be unacceptable.

Solder Alloy 90Pb 8Sn 2Cu

Liquidus Temperature: 307°C
Solidus Temperature: 302°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Average

Electrical Resistivity: 21.79×10^{-6} ohm-cm

Average Bond Strength (lbs)

A. As Soldered Condition
Tested at Room Temperature: 0.95

B. As Soldered Condition
Tested at 200°C: 0.45

C. 200°C for 200 hours condition
Tested at Room Temperature: 0.95

D. 200°C for 200 Hours Condition
Tested at 200°C: 0.41

Metallurgical Compatibility Rating

A. Copper Base Material: Average

B. Au-Plated Kovar Material: Average

Comments and Conclusions

A. The 2 percent copper addition had little more effect on intermetallic compound growth rate reduction than did the 0.5 percent addition in the 89.5 Pb 10Sn 0.5Cu solder alloy.

B. Since the respective bond strength results remained unchanged, it was concluded that the high temperature exposure (200°C for 200 hours) had little effect in changing the as soldered bond strength properties.

C. Since the high temperature bond strength properties are only 50 percent of the room temperature properties, this alloy was considered to have poor high temperature properties and is therefore considered to be unacceptable.

Solder Alloy 93Pb 5Sn 2Zn

Liquidus Temperature: 301°C
Solidus Temperature: 295°C

Solderability Rating

A. Copper Surface: Fair

B. Au Plated Kovar Surface: Good

C. Kovar Surface: De-wet

Electrical Resistivity: 20.39×10^{-6} ohm-cm

Average 45° Bond Strength (lbs.)

A. As Soldered Condition
Tested at Room Temperature: 1.20

B. As Soldered Condition
Tested at 200°C: 0.75

C. 200°C for 200 Hours Condition
Tested at Room Temperature: 1.53

D. 200°C for 200 Hours Condition
Tested at 200°C: 0.75

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Poor

Comments and Conclusions

A. Since the respective bond strength results remained unchanged it was concluded that the high temperature exposure (200°C for 200 hours) had little effect in changing the as soldered bond strength properties.

B. This alloy only marginally wet a copper surface and failed to wet a Kovar surface. It is therefore considered to be unacceptable.

Solder Alloy 90Pb 9Sn 1Zn

Liquidus Temperature: 290°C
Solidus Temperature: 282°C

Solderability Rating

A. Copper Surface: Fair

B. Au-Plated Kovar Surface: Excellent

C. Kovar Surface: De-wet

Electrical Resistivity: 20.94×10^{-6} ohm-cm

Average 45° Bond Strength (lbs)

A. As Soldered Condition
Tested at Room Temperature: 1.05

B. As Soldered Condition
Tested at 200°C: 0.67

C. 200°C for 200 Hours Condition
Tested at Room Temperature: 1.12

D. 200°C for 200 Hours Condition
Tested at 200°C: 0.55

Metallurgical Compatibility

A. Copper Base Material: Good

B. Au-Plated Kovar Base Material: Average

Comments and Conclusions

A. The lead-tin-zinc solder alloys suffered the same 50 percent reduction in respective condition bond strength properties as did the lead-tin-copper alloys.

B. This alloy only marginally wet a copper surface and failed to wet a Kovar surface and is therefore considered to be unacceptable.

Solder Alloy 89.5Pb 10Cd 0.5Cu

Liquidus Temperature: 277°C
Solidus Temperature: 250°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Poor

C. Kovar Surface: Average

Electrical Resistivity: 15.82×10^{-6} ohm-cm

Average 45° Bond Strength (lbs)

A. As Soldered Condition
Tested at Room Temperature: 1.24

B. As Soldered Condition
Tested at 200°C: 0.52

C. 200°C for 200 Hours Condition
Tested at Room Temperature: 1.60

D. 200°C for 200 Hours Condition
Tested at 200°C: 0.81

Metallurgical Compatibility

A. Copper Base Material: Average

B. Au-Plated Kovar Base Material: Average

Comments and Conclusions

A. The 0.5 percent copper content of this alloy seemed to reduce the intermetallic compound growth rate on a copper surface when compared to the lead-cadmium alloys of Task I.

B. The 200°C bond strength testing temperature reduced the room temperature property by 50 percent. This reduction, as previously noted, is also observed for the lead-tin-copper and lead-tin-zinc alloys.

Solder Alloy 90Pb 8Cd 2Cu

Due to the relatively high copper content, this alloy proved to be too viscous and was therefore eliminated from the Task II candidate alloy list. Excessive amounts of $CuCd_3$ intermetallic compound particles formed when the alloy was originally prepared which hampered flow during subsequent melting (Figure 41).

Solder Alloy 90Pb 9Cd 1Zn

Liquidus Temperature: 260°C
Solidus Temperature 238°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Fair

Electrical Resistivity: 17.69×10^{-6} ohm-cm

Average 45° Bond Strength (lbs)

A.	As Soldered Condition Tested at Room Temperature:	0.64
B.	As Soldered Condition Tested at 200°C:	0.59
C.	200°C for 200 Hours Condition Tested at Room Temperature:	1.13
D.	200°C for 200 Hours Condition Tested at 200°C:	0.78

Metallurgical Compatibility

A. Copper Base Material: Excellent

B. Au-Plated Kovar Base Material: Good

Comments and Conclusions

A. The 200°C testing temperature did not significantly reduce the high temperature bond strength properties. This particular alloy has good room temperature strength properties, excellent elevated temperature strength properties, good electrical conductivity and adequate solderability characteristics. Therefore, it was selected as one of the solder alloys to be studied during Task III.

B. This alloy proved to be completely stable at elevated temperatures and compatible with copper and gold plated Kovar systems. The 200 hour exposure at 200°C significantly increased the respective bond strength properties. Table 15 shows the failure mode changing from the lead to solder interface for the "as soldered" condition to a pure solder failure mode after exposure.

C. **Figure 44 (view a) shows the wetting reaction on a copper surface to be the formation of CuZn (approximate composition) and the $Cu_3Cd_3Zn_4$ ternary intermetallic compound to form during high temperature exposure. The $Cu_3Cd_3Zn_4$ reaction occurs as readily in a lead matrix as in a cadmium matrix (Figures 44 and 35). View b of Figure 44 reveals the minor extent of intermetallic compound formation following high temperature exposure.**

D. **Figure 45 (view a) shows the wetting reaction on a gold plated Kovar surface to be the formation of $AuZn_3$ intermetallic compound. View b reveals the primary reaction to be the formation of $AuZn_3$ followed by a secondary dissolution reaction with the excess cadmium in the solder alloy. This secondary reaction tends to lift the previously formed $AuZn_3$ from the surface of the Kovar base material. Subsequent tests indicate that this lifting of $AuZn_3$ phase does not adversely affect the overall performance or properties of the solder alloy.**

Solder Alloy 93Pb 5Cd 2Zn

Liquidus Temperature: 287°C
Solidus Temperature: 245°C

Solderability Rating

A. Copper Surface: Average

B. Au-Plated Kovar Surface: Good

C. Kovar Surface: Poor

Electrical Resistivity: 18.87×10^{-6} ohm-cm

Average 45° Bond Strength (lbs)

A. As Soldered Condition
Tested at Room Temperature: 0.95

B. As Soldered Condition
Tested at 200°C. 0.61

C. 200°C for 200 Hours Condition
Tested at Room Temperature: 1.32

D. 200°C for 200 Hours Condition
Tested at 200°C: 0.66

Metallurgical Compatibility

A. Copper Base Material: Average
B. Au-Plated Kovar Base Material: Good

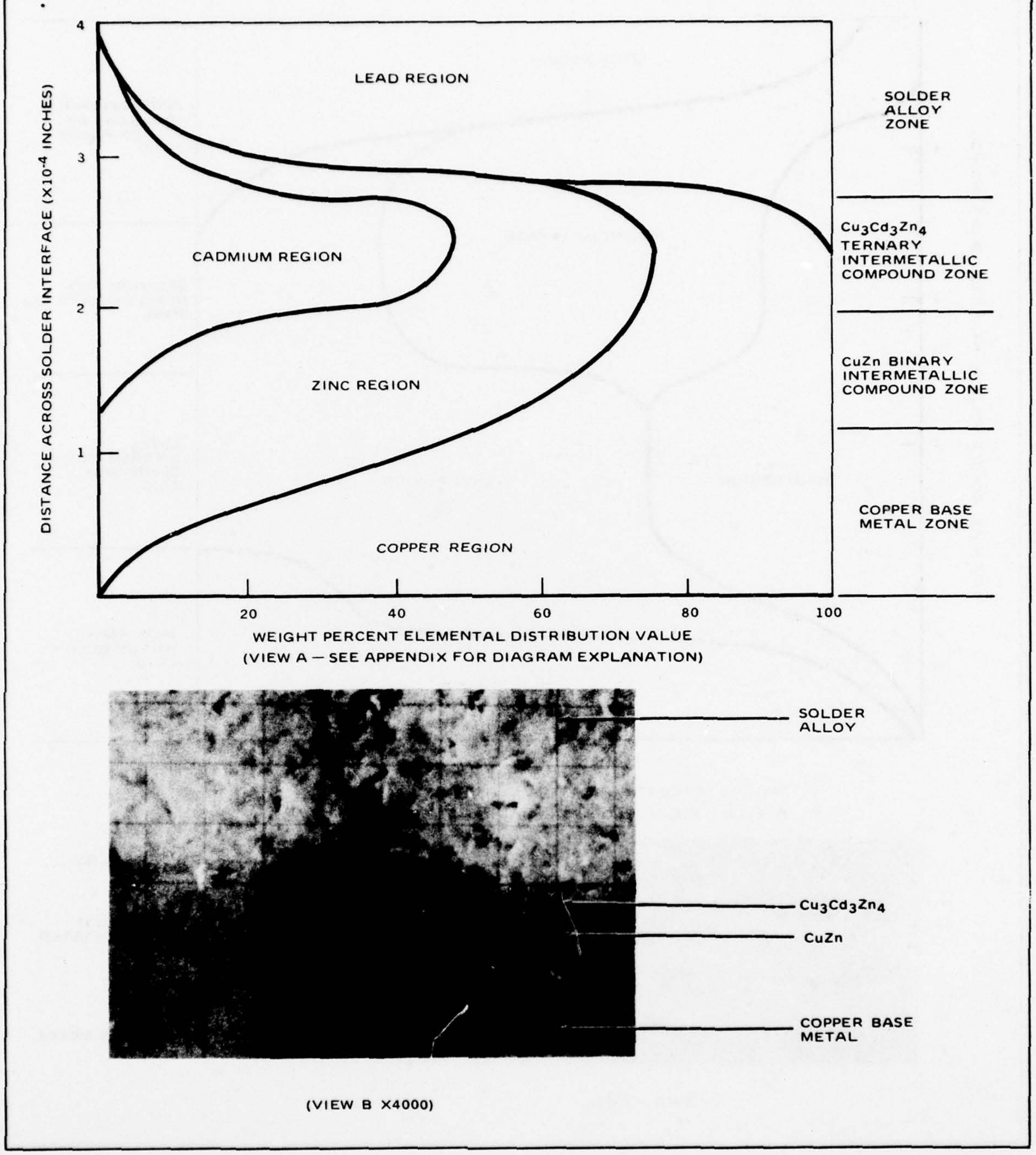


Figure 44. Copper Surface 90 Pb 9 Cd 1 Zn Solder Alloy Interface Reaction (Following Exposure to 200°C for 200 Hours

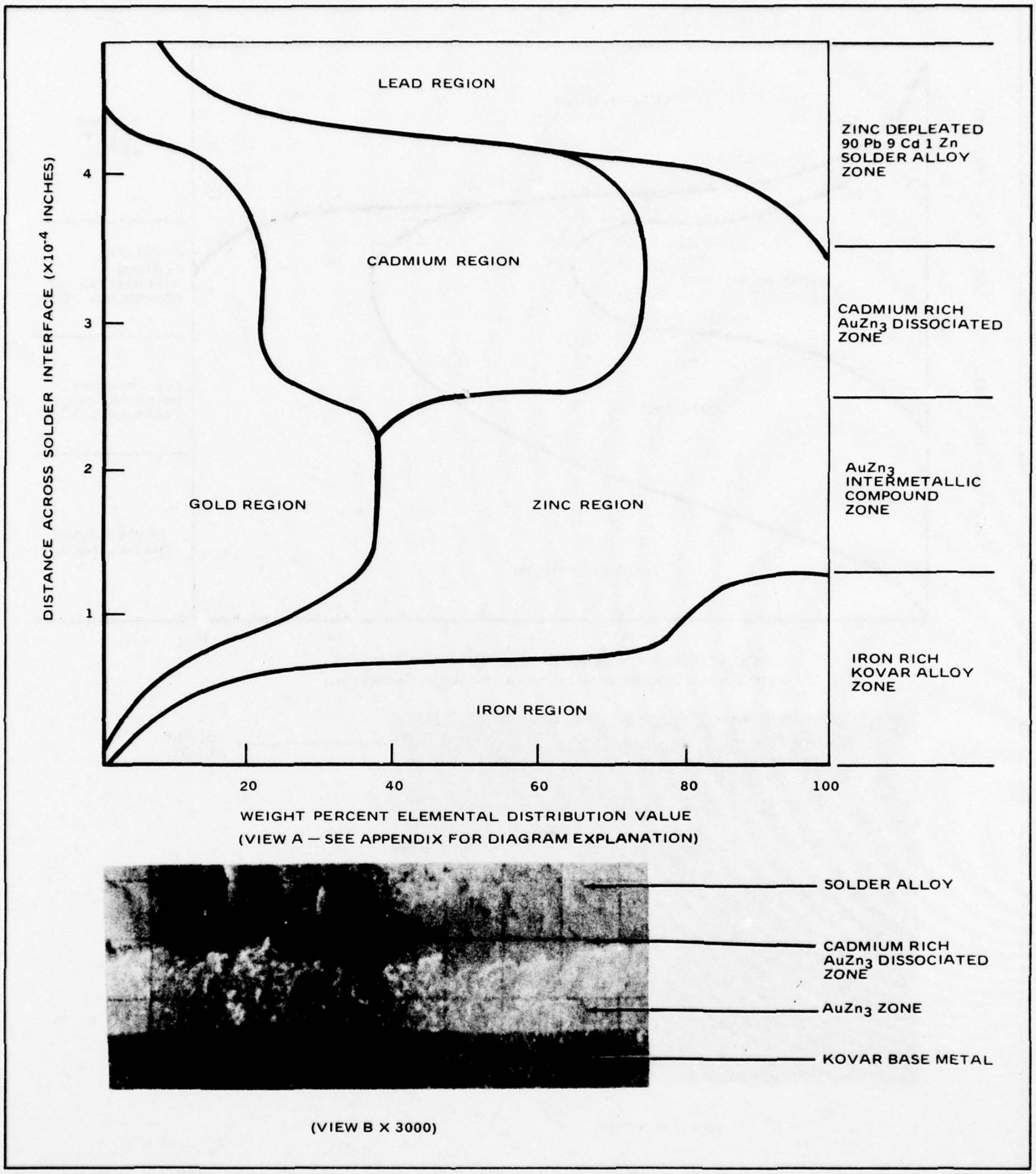


Figure 45. Gold Plated Kovar Surface 90 Pb 9 Cd 1 Zn Solder Alloy Interface Reaction (Following Exposure to 200°C for 200 Hours)

TABLE 19. TERNARY ALLOY CHARACTERIZATION SCREENING RESULTS

Solder Alloy	Solderability			Mechanical Bond Strength			
				As Soldered Condition		Exposed Condition	
	Copper Surface	Kovar Surface	Au-Kovar Surface	$20^{o}C$ Testing Temperature	$200^{o}C$ Testing Temperature	$20^{o}C$ Testing Temperature	$200^{o}C$ Testing Temperature
89.5Pb 10Sn 0.5Cu	6	4	4	7	6	7	6
90Pb 8Sn 2Cu	6	3	4	8	6	7	5
93Pb 5Sn 2Zn	2	0	4	9	10	10	9
90Pb 9Sn 1Zn	3	0	4	10	9	8	7
89.5Pb 10Cd 0.5Cu	6	3	1	10	7	10	10
90Pb 9Cd 1Zn	7	2	4	6	8	8	10
93Pb 5Cd 2Zn	7	1	4	8	8	9	8
Maximum Weight Value	10	5	5	10	10	10	10

TABLE 19. TERNARY ALLOY CHARACTERIZATION SCREENING RESULTS (Continued)

Solder Alloy	Metallurgical Compatibility		Electrical Resistivity	Cost	Toxicity	Total
	Copper Surface	Au-Kovar Surface				
89.5Pb 10Sn 0.5Cu	5	2	1	2	5	55
90Pb 8Sn 2Cu	6	2	2	2	5	56
93Pb 5Sn 2Zn	7	2	2	4	5	64
90Pb 9Sn 1Zn	8	2	2	3	5	61
89.5Pb 10Cd 0.5Cu	4	3	4	2	3	63
90Pb 9Cd 1Zn	10	5	3	3	3	69
93Pb 5Cd 2Zn	3	3	2	4	4	61
Maximum Weight Value	10	5	5	5	5	90

Comments and Conclusions

A. Due to twice the zinc content, this alloy produces twice as much $Cu_3Cd_3Zn_4$ intermetallic compound at a copper interface than does the 90Pb 9Cd 1Zn solder alloy. It is therefore concluded that the optimum zinc content for lead-cadmium-zinc solder alloys is within the 0.5 to 1.0 percent range. If the zinc composition is maintained in this range the $Cu_3Cd_3Zn_4$ intermetallic barrier is formed without producing excessive and detrimental phases at the solder interface.

B. A more significant drop in strength at high temperature occurred with this alloy than with the 90 Pb 9Cd 1 Zn solder alloy.

CONCLUSIONS

The test data reveals that the 90Pb 9Cd 1 Zn alloy forms the least amount of intermetallic compound during high temperature exposure. It was discovered during the Task I and Task II efforts that small amounts of zinc in the presence of cadmium will form the $Cu_3Cd_3Zn_4$ (approximate atomic composition) ternary intermetallic compound on a copper surface during extended exposure to elevated temperatures. The thickness of this intermetallic layer is entirely dependent on the zinc content of the solder alloy. The higher the zinc concentration the more severe the resulting ternary intermetallic compound formation. This solder alloy forms only 1×10^{-4} inches of intermetallic (Table 16) before the solder immediately adjacent to the copper interface is depleted of zinc content. Once all the accessible zinc is consumed, the ternary reaction subsides. The resulting $Cu_3Cd_3Zn_4$ layer then acts as a barrier thereby precluding subsequent formation of binary cadmium-copper intermetallic compounds. The solder interface is then considered to be inert regardless of continued long term exposure to elevated temperatures. The lead constituent provides excellent elevated temperature properties while the cadmium and zinc constituents increase solderability and minimize the formation of intermetallic compounds.

Since the 90Pb 9Cd 1Zn alloy of Task II proved to be superior it was selected for final evaluation in Task III. It is of interest to compare it to a high temperature lead - tin alloy which also had a high rating in Task I, viz. 90 Pb 10Sn. For these reasons these two alloys were chosen for Task III, the final characterization study.

SECTION 4
TASK III FINAL CHARACTERIZATION STUDY

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DEVELOPMENT OF IMPROVED SOLDERS FOR ELECTRONIC RELIABILITY.(U)
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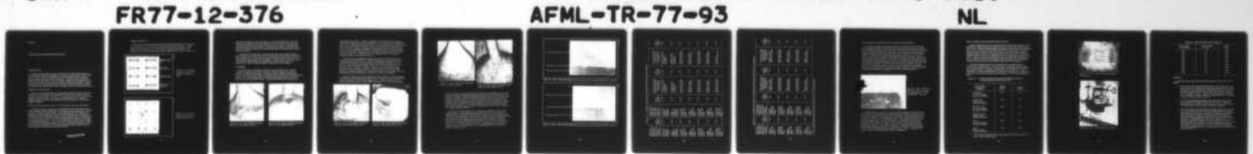

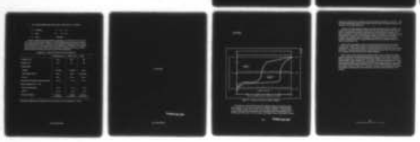

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TASK III FINAL CHARACTERIZATION STUDY

INTRODUCTION

The final characterization study conducted on the alloy systems that were determined to be the most acceptable from Tasks I and II (90 Pb 10 Sn and 90 Pb 9 Cd 1 Zn solder alloys) included tests to determine metallurgical stability, thermal fatigue and shock loading properties. In addition to the two high temperature alloys listed above, control samples soldered with the standard Sn 63 tin-lead solder alloy were subjected to similar metallurgical stability, thermal fatigue and shock loading tests thereby offering a common ground for comparison with the most common solder alloy presently used in the electronics industry.

THERMAL FATIGUE TEST

Bond test and plated through hole type samples soldered with the 90 Pb 10 Sn and 90 Pb 9 Cd 1 Zn alloys were subjected to temperature cycling between the operational limits of 200°C and -55°C. Five hundred cycles were run allowing 10 minutes at the cold station, 22 minutes at the hot station and 4 minutes at ambient conditions prior to and following hot and cold exposure. One cycle is defined as follows:

200°C for 22 min.→20°C for 4 min.→-55°C for 10 min.→20°C for 4 min.→200°C

Periodic in-process samples were withdrawn from the automatic thermal fatigue chamber and examined under the scanning electron microscope. In addition to the SEM surface examination, these plated through hole samples were sectioned so that the internal quality of the plated-through-hole to lead solder interfaces could be established. Samples were withdrawn after completion of 10, 35, 100, 200, 300, 400 and 500 cycles and subsequently evaluated. Bond tests were performed after 10, 35, 100, 300 and 500 cycles to determine any change in bond strength properties. The Sn 63 tin-lead thermal fatigue control samples were subjected to the same thermal cycle test and evaluation schedule as were the 90 Pb 10 Sn and 90 Pb 9 Cd 1 Zn high temperature alloys except the Sn 63 control sample hot station was maintained at 125°C.

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Sample Configuration

Two-sided, 0.062 inch thick polyimide circuit board material was utilized for the 90 Pb 10 Sn, 90 Pb 9 Cd 1 Zn and Sn 63 tin-lead control samples. Figures 46 and 47 illustrate the component side and reverse side respectively of the plated through hole specimens. Bare copper, cadmium plated copper, gold plated Kovar and cadmium plated Kovar lead materials were used. In every case

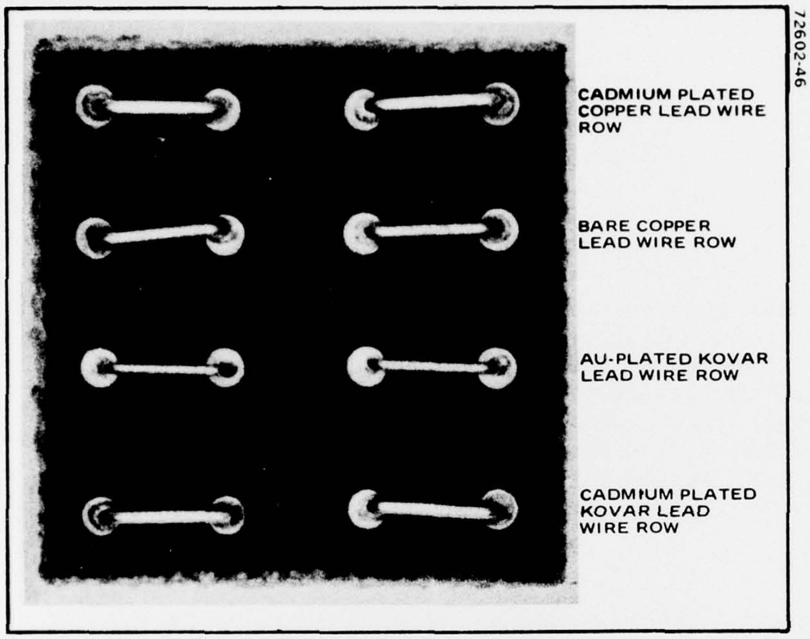

Figure 46. X4. Thermal Fatigue Test Sample Configuration (Component Side).

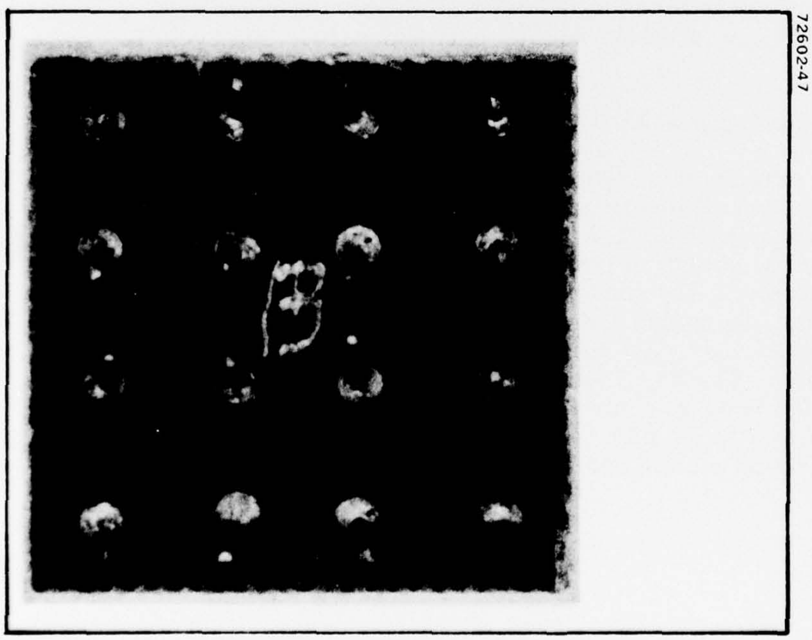

Figure 47. X4. Thermal Fatigue Test Sample Configuration (Reverse Side)

the lead wire diameter was 0.020 inches, the drilled hole diameter was 0.032 inches and the plated-through-hole diameter was 0.029 inches. The lead wire material was soldered to the plated-through-hole and copper clad pads by floating the specimen in molten solder for a period of ten seconds. Type RMA flux per MIL-F-14256 was used and the soldering operation was performed in an inert argon atmosphere.

For purposes of comparison, Sn 63 tin-lead solder alloy control samples were fabricated from two-sided 0.062 inch thick epoxy type circuit board material. These samples were subjected to the same thermal cycle test as the Sn 63 tin-lead polyimide circuit board control samples. In this manner, the thermal expansion property difference between polyimide and epoxy board material was evaluated as related to fatigue cracking during thermal cycle testing.

Test Results

The SEM surface examination of 90 Pb 10 Sn and 90 Pb 9 Cd 1 Zn plated through hole samples show the as soldered conditions (Figures 48 and 49) to be free of cracks and separations. Nominal amounts of interdendritic shrink cavities are evident but are within the normal limits expected for a solidified solder mass. Pad-to-solder separation was first encountered in the 90 Pb 10 Sn samples after 10 thermal fatigue cycles. Subsequent cycling further enlarged and

Figure 48. X50. Typical 90Pb 10Sn Solder Joint in the As Soldered Condition

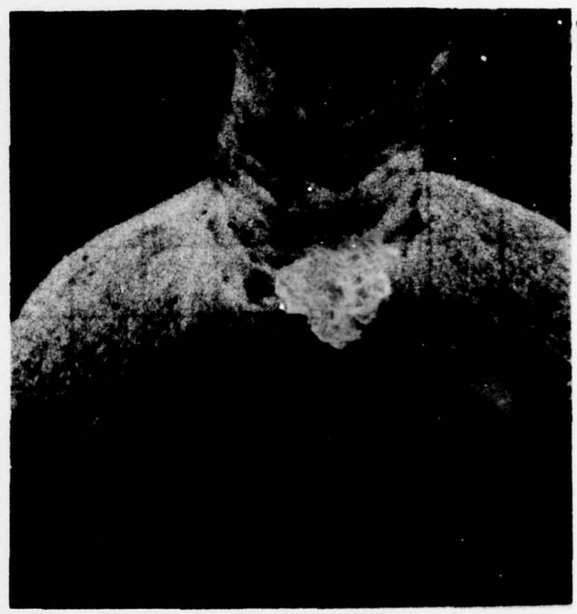

Figure 49. X50. Typical 90Pb 9Cd 1Zn Solder Joint in the As Soldered Condition

aggravated this condition. Figure 50 illustrates a typical 90 Pb 10 Sn solder joint that was subjected to 500 thermal fatigue cycles. Solder alloy cracking and gross pad-to-solder separation are evident. No evidence of pad-to-solder separating or solder alloy fatigue cracking was found in joints soldered with the 90 Pb 9 Cd 1 Zn alloy. Figure 51 illustrates a typical 90 Pb 9 Cd 1 Zn joint following 500 cycles of thermal fatigue testing. The existing interdenritic shrink cavities are no more extensive than those found in samples representing the as soldered condition (Figure 49). Therefore, the cavity shown in Figure 51 probably originated during the soldering operation.

The Sn 63 epoxy and polyimide circuit board solder samples failed the low temperature thermal fatigue test. Figure 52 illustrates a typical crack-free as soldered Sn 63 joint. A normal amount of interdendritic shrink cavity is present. Solder alloy fatigue cracking and solder-to-pad separation was first observed after 200 cycles of testing. Figure 53 shows a typical Sn 63 joint after 500 cycles of testing. The solder mass has separated from the copper clad pad and thermal fatigue cracks are present in the lead wire fillet edge. Some Sn 63 samples cracked more severely than others but all failures occurred independently of the circuit board and lead wire material combination.

The 90 Pb 10 Sn pad-to-solder separation failure (Figure 50) was investigated by comparing cross sections of samples in the as soldered condition with samples that were subjected to 500 thermal fatigue cycles. Figure 54 reveals pad-to-solder separation present in the as soldered condition. It is therefore concluded

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Figure 50. X50. Typical 90Pb 10Sn Solder Joint After 500 Thermal Fatigue Cycles

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Figure 51. X50. Typical 90Pb 9Cd 1Zn Solder Joint After 500 Thermal Fatigue Cycles

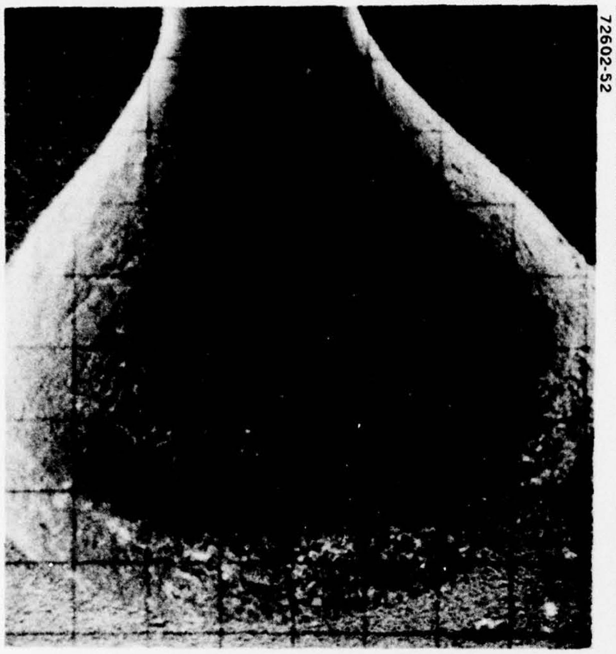

Figure 52. X50. Typical Sn63 Solder Joint in the As Soldered Condition

Figure 53. X50. Typical Sn63 Solder Joint After 500 Thermal Fatigue Cycles

that the separation failure was initially derived during solidification of the 90 Pb 10 Sn alloy and was subsequently aggravated and enlarged during thermal cycle testing. The failure originally propagated through a thin layer of Cu_6 Sn_5 intermetallic compound. Due to the relatively high soldering temperature used for this alloy (330°C minimum), excessive thermal stresses were encountered at the brittle Cu_6 Sn_5 interface during cooling and following solidification. Figure 55 illustrates a 90 Pb 9 Cd 1 Zn solder interface in the as soldered condition. The chemical bond between the copper clad pad and the solder alloy is shown to be complete and free of defects.

Periodic 45° bond strength tests were conducted during the course of the thermal fatigue test utilizing copper and gold plated Kovar lead materials. Table 20 lists the bond strength properties for each circuit board solder alloy and ribbon lead combination. The 90 Pb 10 Sn solder alloy 45° gold plated Kovar lead material bond strength properties were reduced by almost 50 percent following 500 cycles of thermal fatigue testing. The 45° bond strength gold plated Kovar lead properties of the 90 Pb Cd 1 Zn solder alloy increased as a result of thermal fatigue testing by a factor of approximately 25 percent. No significant change in the standard Sn 63 strength properties due to thermal fatigue testing was noted.

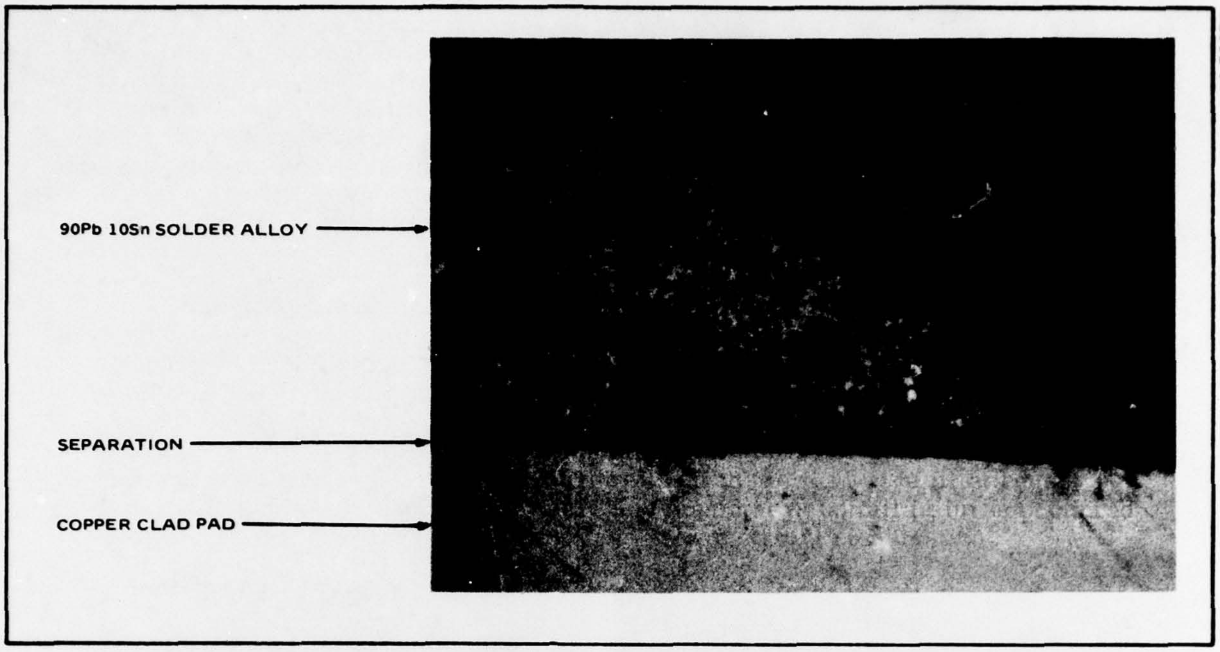

Figure 54. X500 – 90Pb 10Sn Solder Joint Cross-Section in the As Soldered Condition. Unetched.

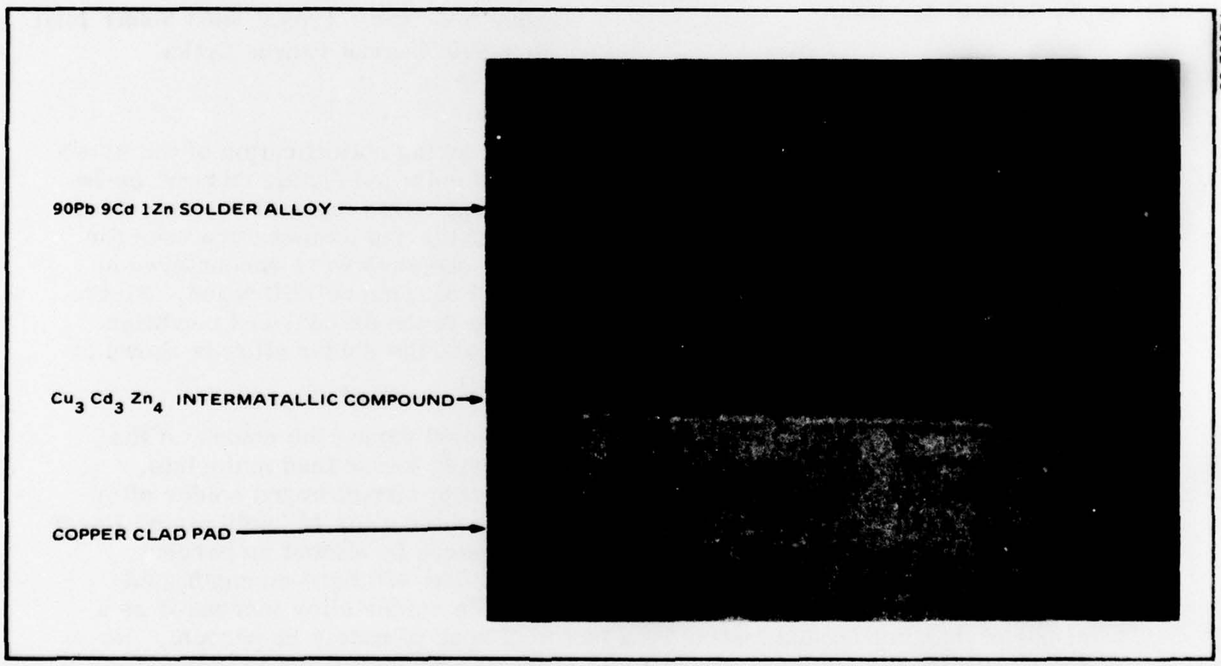

Figure 55. X500 – 90Pb 9Cd 1Zn Solder Joint Cross-Section in the As Soldered Condition. Unetched.

TABLE 20. THERMAL FATIGUE AVERAGE BOND STRENGTH RESULTS

90Pb10Sn Solder Alloy Polyimide Board (Lead Material) (Condition)	Ave. Strength (lbs)*	90Pb9Cd1Zn Solder Alloy Polyimide Board (Lead Material) (Condition)	Ave. Strength (lbs)*	Sn63 Solder Alloy Polyimide Board (Lead Material) (Condition)	Ave. Strength (lbs)*	Sn63 Solder Alloy Epoxy Board (Lead Material) (Condition)	Ave. Strength (lbs)*
Au-Kovar Leads As Soldered Condition	0.78	Au-Kovar Leads As Soldered Condition	0.74	Au-Kovar Leads As Soldered Condition	0.45	Au-Kovar Leads As Soldered Condition	0.54
Copper Leads As Soldered Condition	0.95	Copper Leads As Soldered Condition	1.29	Copper Leads As Soldered Condition	1.95	Copper Leads As Soldered Condition	2.34
Au-Kovar Leads 10 Cycle Condition	0.72	Au-Kovar Leads 10 Cycle Condition	0.68	Au-Kovar Leads After 10 Cycles	0.57	Au-Kovar Leads After 10 Cycles	0.51
Copper Leads 10 Cycle Condition	0.86	Copper Leads 10 Cycle Condition	1.50	Copper Leads After 10 Cycles	1.72	Copper Leads After 10 Cycles	1.81
Au-Kovar Leads 35 Cycle Condition	0.64	Au-Kovar Leads 35 Cycle Condition	0.72	Au-Kovar Leads After 35 Cycles	0.57	Au-Kovar Leads After 35 Cycles	0.48
Copper Leads 35 Cycle Condition	1.11	Copper Leads 35 Cycle Condition	1.62	Copper Leads After 35 Cycles	1.67	Copper Leads After 35 Cycles	1.90
Au-Kovar Leads 100 Cycle Condition	0.74	Au-Kovar Leads 100 Cycle Condition	0.71	Au-Kovar Leads After 100 Cycles	0.49	Au-Kovar After 100 Cycles	0.60

TABLE 20. THERMAL FATIGUE AVERAGE BOND STRENGTH RESULTS (Continued)

90Pb10Sn Solder Alloy Polyimide Board (Lead Material) (Condition)	Ave. Strength (lbs)*	90Pb9Cd1Zn Solder Alloy Polyimide Board (Lead Material) (Condition)	Ave. Strength (lbs)*	Sn63 Solder Alloy Polyimide Board (Lead Material) (Condition)	Ave. Strength (lbs)*	Sn63 Solder Alloy Epoxy Board (Lead Material) (Condition)	Ave. Strength (lbs)*
Copper Leads-100 Cycle Condition	1.06	Copper Leads 100 Cycle Condition	1.36	Copper Leads After 100 Cycles	1.57	Copper Leads After 100 Cycles	2.16
Au-Kovar Leads 300 Cycle Condition	0.53	Au-Kovar Leads 300 Cycle Condition	0.82	Au-Kovar Leads After 300 Cycles	0.47	Au-Kovar Leads After 300 Cycles	0.66
Copper Leads 300 Cycle Condition	1.11	Copper Leads 300 Cycle Condition	1.48	Copper Leads After 300 Cycles	1.74	Copper Leads After 300 Cycles	1.77
Au-Kovar Leads 500 Cycle Condition	0.48	Au-Kovar Leads 500 Cycle Condition	0.83	Au-Kovar Leads After 500 Cycles	0.47	Au-Kovar Leads After 500 Cycles	0.52
Copper Leads 500 Cycle Condition	1.18	Copper Leads 500 Cycle Condition	1.69	Copper Leads After 500 Cycles	1.40	Copper Leads After 500 Cycles	1.68

*The strength values reported are based upon a 0.017 inch lead width

METALLURGICAL STABILITY TEST PROCEDURE AND RESULTS

The high temperature metallurgical stability test (200°C for 500 hours) for the 90 Pb 10Sn and 90Pb 9Cd1Zn solder alloys and the low temperature metallurgical stability test (125°C for 500 hours) for the Sn63 control alloy were performed on lead to plated through hole test samples. The samples were subsequently sectioned and examined to determine the intermetallic compound formation rate on copper. The 90 Pb 10 Sn solder alloy was found to produce 3×10^{-4} inches of $Cu_6\ Sn_5$ intermetallic compound during high temperature exposure. The 90 Pb 9Cd 1 Zn solder alloy formed 5×10^{-5} inches of cadmium rich CuZn intermetallic compound during soldering (Figure 55) and 5×10^{-5} inches of $Cu_3Cd_3Zn_4$ ternary intermetallic compound during high temperature exposure (Figure 56). The Sn63 standard alloy produced 7×10^{-5} inches of $Cu_6\ Sn_5$ intermetallic compound. Since the Sn 63 samples produced relatively small amounts of intermetallic compound during exposure, the $Cu_6\ Sn_5$ intermetallic compound reaction is therefore considered to be extremely sluggish at the 125°C testing temperature.

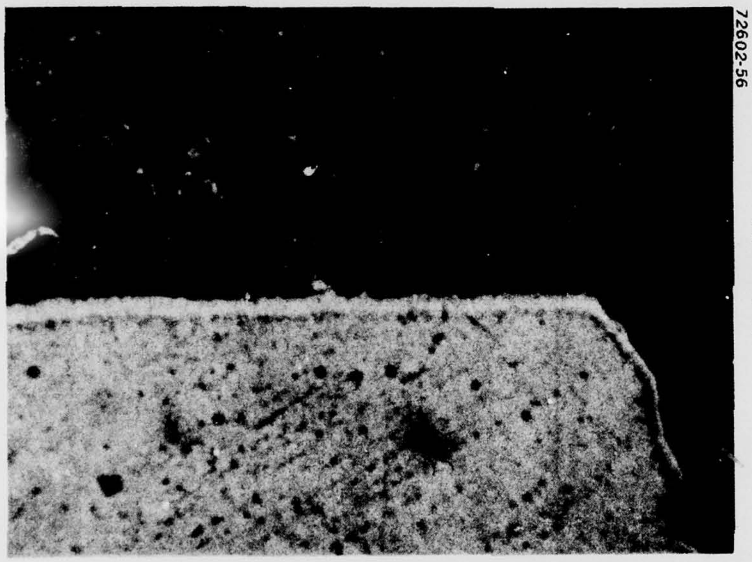

Figure 56. X500 – 90Pb 9Cd 1Zn Solder Joint Cross-Section Following Exposure to 200°C for 500 Hours. Unetched.

Table 21 lists the average 45° bond strength properties of the 90 Pb 10 Sn and 90 Pb 9 Cd 1 Zn solder alloys following exposure to 200°C for 500 hours and the average strength properties for the Sn 63 standard alloy following exposure to 125°C for 500 hours. No significant change in bond strength properties, due to extended exposure to elevated temperatures, was noted for the 90 Pb 10 Sn and Sn 63 solder alloys. The 90 Pb 9 Cd 1 Zn, gold plated Kovar lead bond strength value increased by a factor of approximately 50 percent during high temperature exposure. This apparent increase in strength properties derived during high temperature aging is not completely understood. This phenomenon was also observed during the bond strength testing of Task II and the thermal fatigue testing of Task III (Tables 15 and 20 respectively).

SHOCK LOADING TEST PROCEDURE AND RESULTS

Sample configuration for the mechanical shock loading test consists of a gold plated Kovar flatpack component reflow soldered to a previously solder coated circuit board. The body of the flatpack was bonded to the circuit card with Nomex tape. The previously solder coated gold plated Kovar ribbon leads were subsequently reflow soldered to the solder coated circuit board detail (Figure 57). Samples prepared with Sn 63 on polyimide board material and 90 Pb 10 Sn on polyimide board material were fabricated to the test configuration shown in Figure 57. Samples of each circuit board material and solder alloy combination were mounted on each face of an aluminum alloy fixturing block with an epoxy adhesive and placed in the shock loading apparatus shown in Figure 58.

The shock loading procedure was conducted per the requirements of MIL-STD-883, Method 2002.1. Each face of the testing block shown in Figure 58 was impacted to 5 tension, 5 compression, 10 shearing and 10 peeling type impacts at each of the acceleration levels shown in Table 22. Visual inspection at 10 times magnification was performed following each acceleration level shock series and no evidence of bond failures or solder joint cracking was found.

TABLE 21. AVERAGE BOND STRENGTH TEST RESULTS FOR THE METALLURGICAL STABILITY STUDY

Solder Alloy Lead Material Condition	Ave. Strength (lbs)*	Failure Mode**
90 Pb 10 Sn Au-Kovar Leads 500 hours @ 200°C	0.76	LS
90 Pb 10 Sn Copper Leads 500 hours @ 200°C	1.08	LS
90 Pb 9Cd 1 Zn Au-Kovar Leads 500 hours @ 200°C	0.94	LS
90 Pb 9 Cd 1 Zn Copper Leads 500 hours @ 200°C	1.53	LS
Sn 63 Au-Kovar Leads 500 hours @ 125°C	0.66	LS
Sn 63 Copper Leads 500 hours @ 125°C	1.97	LS

*The reported strength values are based upon a 0.017 inch lead width.
**LS – Lead to solder failure

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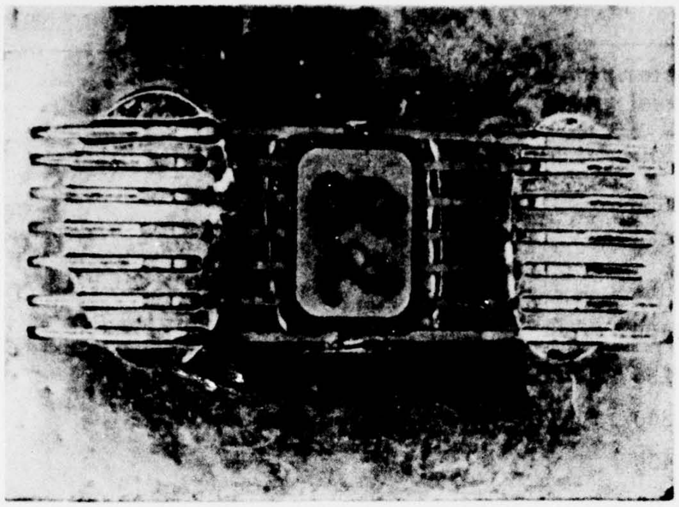

Figure 57. X3.75 – Shock Loading Test Sample Configuration

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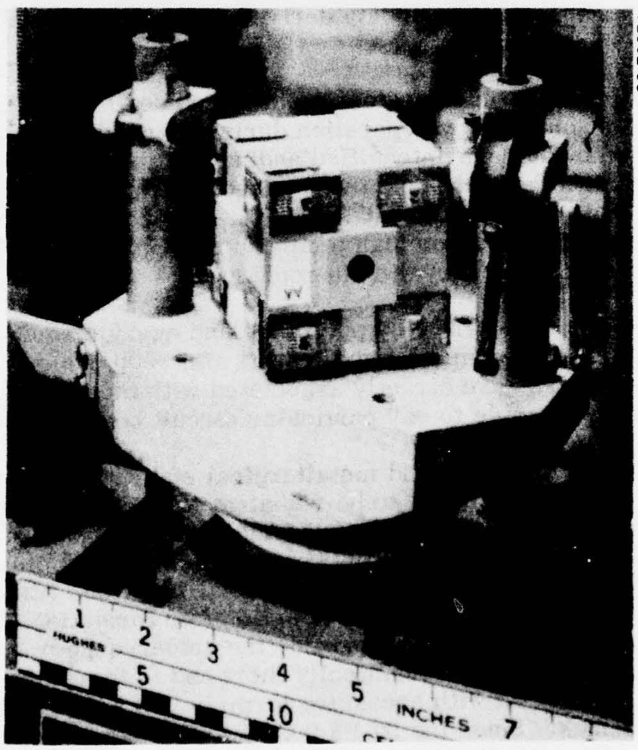

Figure 58. X1/3 – Shock Loading Test Set-Up

TABLE 22. SHOCK LOADING TEST RESULTS

Acceleration G Level (peak)	Pulse Duration (m sec)	Failure Type
1550	0.5	None
1650	0.5	None
1800	0.5	None
1900	0.5	None
2000	0.5	None
2150	0.5	None
2300	0.5	None
2450	0.5	None
2600	0.5	None

SUMMARY

Conclusions based upon the data derived during the Task III effort are as follows:

1. The tin-lead solder system produces solder alloy fatigue cracks and pad-to-solder alloy separation during thermal fatigue testing. These failure modes are intensified and accelerated when the hot station is maintained at 200°C and the tin-lead solder alloy liquidus temperature is in excess of 300°C. The tin-lead solder system is therefore not recommended for high temperature applications where resistance to thermal fatigue cycling is required.

2. The Sn 63 standard alloy polyimide and epoxy circuit board solder joints failed thermal fatigue testing after 200 cycles. Therefore, these failures are directly associated with the Sn 63 solder alloy and are not traceable to any particular circuit board material.

3. The thermal fatigue and metallurgical stability tests prove the 90 Pb 9 Cd 1 Zn solder alloy to be resistant to high temperature thermal fatigue cycling and well suited for elevated temperature applications. This alloy has its own built-in mechanism for terminating solid state intermetallic compound chemical reactions with copper base materials. By controlling the solid state formation of the $Cu_3Cd_3Zn_4$ ternary intermetallic compound, the solder-copper interface is ultimately rendered chemically inert and is therefore immune to failures associated with excessive formation of brittle intermetallic compounds. Since the 90 Pb 9 Cd 1 Zn solder alloy is chemically inert at elevated temperatures, long term solder alloy degradation can be totally avoided.

4. The recommended final solder alloy composition is as follows:

a. Cadmium 8 - 12 wt %

b. Zinc 0.5 - 1.0 wt %

c. Lead Balance

Table 23 illustrates the established properties for the 90 Pb 10 Sn, 90 Pb 9 Cd 1 Zn and Sn 63 solder alloys. A direct comparison of the more critical properties can be made. In addition to the optimum properties shown in Table 23, the 90 Pb 9 Cd 1 Zn alloy is the least expensive as related to raw material cost and since tin is the most costly elemental constituent of the three alloys listed, the Sn 63 eutectic alloy is by far the most expensive.

TABLE 23. FINAL TASK III ALLOY SUMMARY

	90Pb 9Cd 1Zn	90Pb 10Sn	Sn63
Liquidus ($^{\circ}$C)	260	305	182
Solidus ($^{\circ}$C)	238	278	182
Solderability			
Copper	Average	Average	Good
Gold-Plated Kovar	Good	Good	Excellent
Kovar	Fair	Poor	Good
Electrical Resistivity (Microhm-CM)	17.69	20.30	14.73
Bond Strength (45°) - Lbs			
Room Temperature	0.64	1.18	0.55
200°C	0.59	0.60	0.24*
Thermal Fatigue	Passed 500 cycles	Failed (10 cycles)	Failed (200 cycles)*

*All High Temperature Testing for the Sn 63 alloy was at a maximum of 125°C.

APPENDIX

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APPENDIX

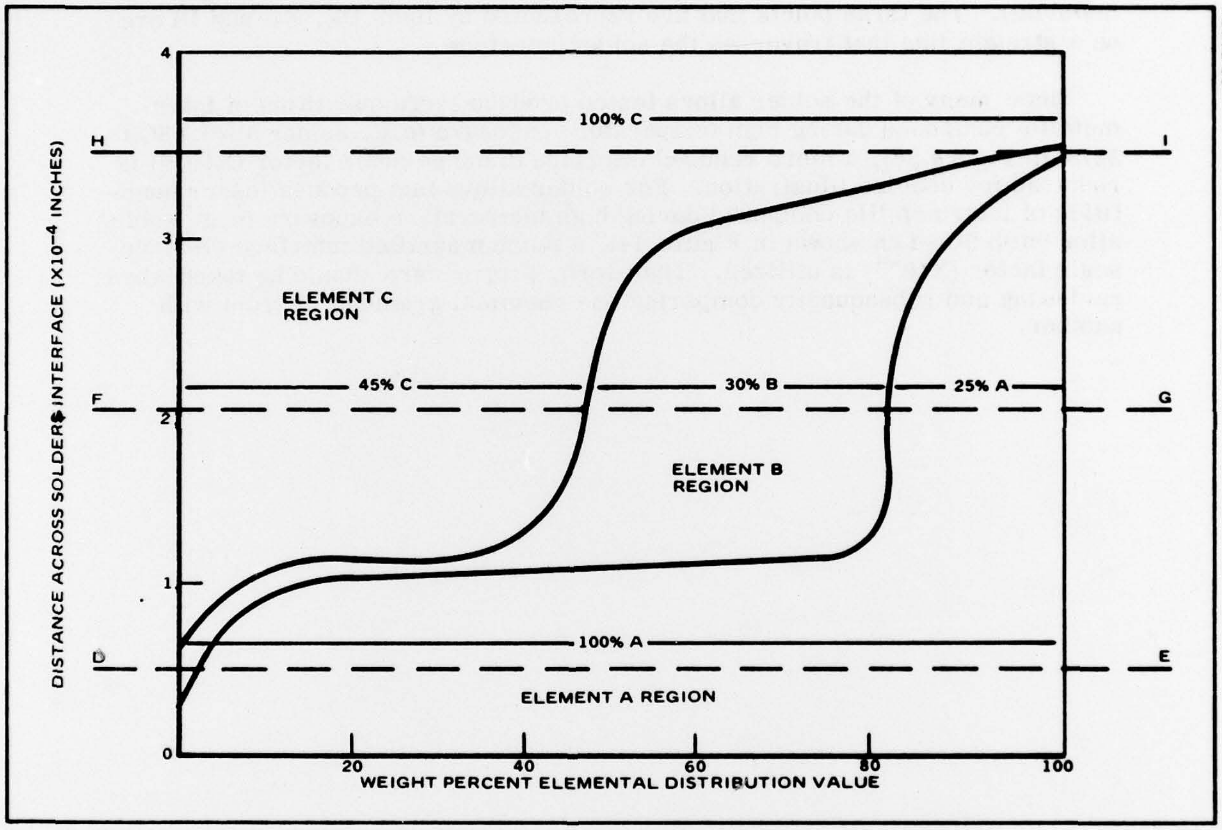

Figure 59. Example of Chemical Gradient Diagram

The purpose of the chemical gradient diagrams shown in the body of the text (Figures 33, 34, 35, 44 and 45) is to present a pictorial representation of the change in chemistry across various solder interfaces. In this manner, specific intermetallic compounds can be identified and corresponding layer thicknesses determined. For example, the diagram above represents a solder

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interface cross section consisting of three metallic elements A, B and C. The line DE constitutes a point in the solder interface that is composed entirely of element A (e.g. base material).

The line FG represents a point in the solder interface that is located, in a transverse direction, 0.00015 inches from the point described by the line DE. Line FG reveals the chemical composition at this particular location to be 25wt.% element A, 30wt.% element B and 45wt.% element C (100% total). This composition is shown to remain constant between the interface distances of 0.00010 and 0.00030 inches. Therefore, this particular zone is an intermetallic compound layer 0.00020 inches thick that is composed of 25wt.% A, 30wt.% B and 45wt.% C.

The line HI represents a point in the sectioned interface that is located 0.00030 and 0.00015 inches from the points described by lines DE and FG respectively. This point is shown to consist entirely of element C (e.g. solder material). The three points that are represented by lines DE, FG and HI are on a straight line that traverses the solder interface.

Since many of the solder alloys tested produce large quantities of intermetallic compound during high temperature exposure (e.g. solder alloy 68Cd 32Zn in Figure 34), a more reduced interface distance scale factor ($X10^{-3}$) is required for concise illustration. For solder alloys that produce lesser quantities of intermetallic compound during high temperature exposure (e.g. solder alloy 90Pb 9Cd 1Zn shown in Figure 44), a more magnified interface distance scale factor ($X10^{-4}$) is utilized. Therefore, proper care should be taken when reviewing and subsequently comparing one chemical gradient diagram with another.

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